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Direct Spin-Lattice Relaxation Processes*

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A spin-lattice Hamiltonian for direct processes (the dynamic spin Hamiltonian) is defined which contains the effective spin operator and nuclear spin operator used in the static spin Hamiltonian. From the form of the dynamic Hamiltonian, certain combinations of the lattice operators can be identified as the dynamic analog of the static spin Hamiltonian parameters. The direct relaxation rates can be expressed in terms of spectral densities of the products of the dynamic spin Hamiltonian parameters. Assuming that the interaction of the ion with the crystal is adequately described by a crystal field, the sources of which are characterized by a symmetry group, it is possible to express the spectral densities involved in the spin-lattice relaxation in terms of the spectral densities of the normal modes of the complex. We use the symmetry of the complex and the crystal to limit the number of independent spectral densities of the normal modes without making any detailed assumptions about the lattice phonons nor the way that the sources of the crystal field participate in the lattice vibrations. Particular attention is given to the case of a Kramers doublet with hyperfine structure, and the matrix elements of the spin-lattice Hamiltonian between the eigenstates of the static spin Hamiltonian are given explicitly. These results are applied to the case of divalent cobalt in a nearly cubic field, and it is found that all twenty two of the relaxation rates between levels for which the energy separation is $\sim g\beta H$ for any direction of the applied field may be expressed in terms of four constants if the nuclear quadrupole interaction is ignored. The effect of the dynamic hyperfine interaction is found to be surprisingly large. Since all of the relaxation rates depend on the direction of the applied magnetic field, the four constants can be vastly overdetermined by experimental measurements of the direct relaxation processes.

I. GENERAL THEORY

Several recent theoretical papers[1–4] have done much to suggest decisive experiments for the clarification of the spin-lattice relaxation processes in paramagnetic salts. The present paper is an extension (with some modifications) of that work to a discussion of the direct relaxation processes which can occur in a dilute paramagnetic salt with resolved hyperfine structure. These relaxation processes, which are important in dynamic nuclear orientation experiments, have been treated in a phenomenological manner by Abragam[5] and in more detail but in the same spirit by Jeffries.[6] The present treatment is an effort to relate these processes to the more fundamental processes of lattice vibrations.

In Sec. 1, we begin with a discussion of the dynamic crystal field which parallels that given by Van Vleck[7] and, for the most part, serves to define our notation. We conclude Sec. 1 with a definition of the dynamic spin Hamiltonian in a way that is suitable for the treatment of a wide variety of problems. In Sec. 2, the relaxation rates between the eigenstates of the static spin Hamiltonian are calculated and expressed in terms of the spectral densities of the products of the dynamic spin Hamiltonian parameters which have a semiclassical interpretation that is frequently stressed in discussions of nuclear magnetic relaxation.[8] In this section, the spectral densities of the products of the spin Hamiltonian parameters are formally related to those for the products of the normal modes of the complex which is assumed to produce the crystal field. We discuss the relation of the number of independent spectral densities to the symmetry group of the complex and the over-all crystal symmetry which is reflected in the properties of the lattice vibrations. Sec. 3 is more specialized, and is devoted to the detailed evaluation of the matrix elements of the dynamic spin Hamiltonian for a Kramers doublet with electric and magnetic hyperfine interactions and a strong external magnetic field. In part II, we apply the method to divalent cobalt in a nearly cubic field.

1. Spin-Lattice Hamiltonian

From the point of view of crystal field theory, the energy levels of ions in crystals are eigenstates of the Hamiltonian

$$W_T = W_I + V_0 + \beta \mathbf{H} \cdot (\mathbf{L} + 2\mathbf{S}), \tag{1}$$

where W_I is the Hamiltonian for the free ion and V_0 is the static crystal field. The spin Hamiltonian is useful when a restricted set of the eigenstates of W_T, say ψ_{hk} (where $h=1, 2, \cdots, 2S+1$ and $k=1, 2, \cdots, 2I+1$), are isomorphous with a set of functions

$$\phi_{hk} = \sum_{mm'} C_{hkmm'} |Sm\rangle |Im'\rangle, \tag{2}$$

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[1] R. D. Mattuck and M. W. D. Strandberg, Phys. Rev. **119**, 1204 (1960).

[2] R. Orbach, Proc. Roy. Soc. (London) **A264**, 458 (1961).

[3] R. Orbach, Proc. Phys. Soc. (London) **77**, 821 (1961).

[4] C. B. P. Finn, R. Orbach, and W. P. Wolf, Proc. Phys. Soc. (London) **77**, 261 (1961).

[5] A. Abragan, Phys. Rev. **98**, 1792 (1955).

[6] C. D. Jeffries, Phys. Rev. **117**, 1056 (1960).

[7] J. H. Van Vleck, Phys. Rev. **57**, 426 (1940).

[8] A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon Press, Oxford, 1961), Chaps. VIII and IX.

which are linear combinations of the products of eigenfunctions of the effective spin operator **S** and the nuclear spin operator **I**. The spin Hamiltonian $\mathcal{H}_S$ is a function of **I** and **S** such that[9,10]

$$\langle\psi_{hk}|W_T|\psi_{hk}\rangle=\langle\phi_{hk}|\mathcal{H}_S|\phi_{hk}\rangle. \tag{3}$$

The coupling between the ions and the lattice vibrations in the crystal field view is produced by the modulation of the crystal field by the motion of the sources relative to the paramagnetic ion. We assume that the sources of the crystal field are a number of nearby molecules or ions which, together with the paramagnetic ion, we designate as a complex without any implications concerning the nature of the chemical bonding. If one describes the motion of the sources in terms of a set of generalized coordinates $Q_j^{(\lambda)}$, the dynamic crystal potential to first order in the displacements from the equilibrium positions is

$$V'(r)=\sum_{j\lambda}\left(\frac{\partial V(r)}{\partial Q_j^{(\lambda)}}\right)Q_j^{(\lambda)}=\sum_{j\lambda}V_j^{(\lambda)}(r)Q_j^{(\lambda)}, \tag{4}$$

where $V_j^{(\lambda)}(r)$ are operators in the space of the ionic wave functions and the generalized displacements are functions of the lattice phonon operators

$$Q_j^{(\lambda)}=\sum_{\mathbf{K}p\omega}Q_j^{(\lambda)}(\mathbf{K}p\omega)=\sum_{\mathbf{K}p\omega}d_j^{(\lambda)}(\mathbf{K}p\omega)(a_{\mathbf{K}p\omega}+a_{\mathbf{K}p\omega}^{\dagger}), \tag{5}$$

in which **K** is a unit vector in the direction of propagation of the phonon, ω is the angular frequency, and p is the polarization index. The choice of the generalized coordinates for describing the motion of the sources relative to the paramagnetic ion will depend not only on the nature of the complex but on the symmetry of the lattice vibrations which are the driving force for the displacements.

The evaluation of spin-lattice relaxation rates between the states (h,k) and (h',k') requires the calculation of $\langle i|\langle\Psi_{hk}|V'|\psi_{h'k'}\rangle|f\rangle$, where $|i\rangle$ and $|f\rangle$ are lattice states. We wish to replace this calculation by the analogous one for the states ϕ_{hk}, with the use of a spin-lattice Hamiltonian defined so that

$$\langle i|\langle\psi_{hk}|V'|\psi_{h'k'}\rangle|f\rangle=\langle i|\langle\phi_{hk}|\mathcal{H}_{SL}|\phi_{h'k'}\rangle|f\rangle, \tag{6}$$

where it is clear that $\mathcal{H}_{SL}$ will contain the nuclear spin and effective spin operators as well as lattice operators.

Mattuck and Strandberg[1] have given an explicit calculation of a spin-lattice Hamiltonian [their Eq. (44)] for an ion with an orbital singlet lowest and no hyperfine structure which is almost, but not quite, in the form required by our definition. Their Hamiltonian contains a quantity $g_{kk'}$ and an operator $\boldsymbol{\mathcal{E}}$ which we would replace by equivalent operators in the effective spin.

Aside from the presence of lattice operators $\mathcal{H}_{SL}$ is precisely the same as the change $\mathcal{H}_S'$ in the static spin Hamiltonian under a static crystal-field perturbation of the same form as V'. This correspondence is very useful in the estimation of the importance of the terms in $\mathcal{H}_{SL}$. For example, if it is known experimentally or theoretically that the hyperfine interaction is more sensitive to the crystal field than the Zeeman splitting (at some fixed applied field), then the hyperfine interaction may dominate the direct spin-lattice relaxation.

For the remainder of this section, we assume that the spin-lattice Hamiltonian has been calculated according to the scheme described above. In order to keep the complexity of notation to a minimum consistent with the discussion of the effects of the hyperfine structure, we shall restrict our considerations to the case in which the lowest eigenfunctions of W_T are a Kramers doublet with hyperfine structure. The static spin Hamiltonian will have the form

$$\mathcal{H}_S=\beta\mathbf{H}\cdot\mathbf{g}\cdot\mathbf{S}+\mathbf{I}\cdot\mathbf{A}\cdot\mathbf{S}+\mathbf{I}\cdot\mathbf{P}\cdot\mathbf{I}, \tag{7}$$

where the effective spin S is one-half. The parameters **g**, **A**, and **P** are second rank tensors. The number of independent components of these tensors is restricted by the symmetry of the static crystal field. The dynamic spin Hamiltonian will have the form

$$\mathcal{H}_{SL}=\beta\mathbf{H}\cdot\mathbf{g}'\cdot\mathbf{S}+\mathbf{I}\cdot\mathbf{A}'\cdot\mathbf{S}+\mathbf{I}\cdot\mathbf{P}'\cdot\mathbf{I}. \tag{8}$$

The second rank tensors $\mathbf{g}'$, $\mathbf{A}'$, and $\mathbf{P}'$ in the present approximation are linear functions of the phonon operators. It is desirable to write (8) in a more compact notation

$$\mathcal{H}_{SL}=\sum_{\alpha ij}U_{ij}^{(\alpha)}M_{ji}^{(\alpha)}, \tag{9}$$

where α takes on the values **g**, **A**, and **P**. $U_{ij}^{(\alpha)}$ are spin operators and $M_{ij}^{(\alpha)}$ are linear combinations of phonon operators. Rather than expand the latter directly in terms of phonon operators, it is more useful for our work in the next section to consider the expansion in the generalized coordinates of the complex:

$$M_{ij}^{(\alpha)}=\sum_{\lambda r}N_{ijr\lambda}^{(\alpha)}Q_r^{(\lambda)}. \tag{10}$$

This is also the form in which the results will be obtained if the perturbation V' is applied in the form given by (4).

2. Spectral Densities and the Utilization of Symmetry

We assume that the general features of the statistical aspects of spin-lattice relaxation are familiar.[8] The transition rate per unit population from a level a to a level b of a spin system is related to that for the reverse process by

$$W_{a\to b}=W_{b\to a}[\exp(E_a-E_b)/kT], \tag{11}$$

where T is the lattice temperature. Abragam[8] has

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[9] W. Low, in *Solid State Physics* (Academic Press Inc., New York (1960), Suppl. II.

[10] G. F. Koster and H. Statz, Phys. Rev. **113**, 445 (1959).

shown that

$$W_{a\to b}=\left(\frac{1}{h}\right)\sum_{\alpha\beta ijlm}\Bigg\{\left[\langle a|U_{ij}{}^{(\alpha)}|b\rangle\langle b|U_{lm}{}^{(\beta)\dagger}|a\rangle\right]\times\Bigg[\frac{1}{N_0}\sum_{ef}\langle eM_{ji}{}^{(\alpha)}|f\rangle\langle f|M_{ml}{}^{(\beta)\dagger}|e\rangle\times e^{-(Ee/kt)}\delta(E_e-E_f+\hbar\omega)\Bigg]\Bigg\},\quad(12)$$

in which $N_0=\sum_e\exp(-E_e/kT)$, $\hbar\omega_0=E_a-E_b$, and the sums will include integrals over continuous spectra. After the average over the initial states $|e\rangle$ and summing over final states $|f\rangle$ of the lattice, one may write

$$W_{a\to b}=\left(\frac{1}{h}\right)\sum_{\alpha\beta ijlm}J_{ij;lm}{}^{(\alpha\beta)}(\omega)\times\langle a|U_{ij}{}^{(\alpha)}|b\rangle\langle b|U_{lm}{}^{(\beta)\dagger}|a\rangle,\quad(13)$$

where

$$J_{ij;lm}{}^{(\alpha\beta)}(\omega)=\sum_p\int d\Omega_{\mathbf{K}}\langle n_{\mathbf{K}p\omega}+1|M_{ji}{}^{(\alpha)}|n_{\mathbf{K}p\omega}\rangle\times\langle n_{\mathbf{K}p\omega}|M_{ml}{}^{(\beta)\dagger}|n_{\mathbf{K}p\omega}+1\rangle\rho_p(\mathbf{K},\omega_0)\quad(14)$$

is called the spectral density tensor for the α and β components of the dynamic spin Hamiltonian. $\rho_p(\mathbf{K},\omega)$ is the density of phonon states per unit energy interval and per unit solid angle with the polarization p, and $d\Omega_{\mathbf{K}}$ is a differential solid angle in the direction $\mathbf{K}$. The state vectors $|n_{\mathbf{K}p\omega}\rangle$ are representations of the lattice states labeled by the number of phonons in each mode. Since the thermal average has been taken already, the squares of the matrix elements of the lattice operators between these states are

$$|\langle n_{\mathbf{K}p\omega}|a_{\mathbf{K}p\omega}|n_{\mathbf{K}p\omega}+1\rangle|^2=[1-\exp(-h\omega/kT)]^{-1}.\quad(15)$$

Substituting (10) into (14), we obtain

$$J_{ij;lm}{}^{(\alpha\beta)}=\sum_{rs\lambda\mu}N_{jir\lambda}{}^{(\alpha)}N_{mls\mu}{}^{(\beta)}[Q_r{}^{(\lambda)},Q_s{}^{(\mu)}]_\omega,\quad(16)$$

where

$$[Q_r{}^{(\lambda)},Q_s{}^{(\mu)}]_\omega=\sum_p\int d\Omega_K\rho_p(\mathbf{K},\omega)\langle n_{Kp\omega}|Q_r{}^{(\lambda)}|n_{Kp\omega}+1\rangle\times\langle n_{Kp\omega}+1|Q_s{}^{(\mu)\dagger}|n_{Kp\omega}\rangle\quad(17)$$

are the spectral densities for the products of the generalized coordinates.

In a semiclassical view of the lattice, the spectral densities defined in (14) would be the Fourier transform of the correlation function of the time-dependent spin Hamiltonian parameters. Our spectral density is defined for those transitions in which the lattice absorbs energy. In the limit of infinite lattice temperature, the spectral densities for absorption and emission of energy by the lattice are the same and agree with the semiclassical result. The spectral densities defined by (17) have a corresponding interpretation.

We consider the situation in which the complex is characterized by a symmetry group G_1 and the crystal by the symmetry group G_2, and we further assume that one of these groups is a subgroup of the other. It is then clearly permissible to choose the generalized coordinates so that $Q_j{}^{(\lambda)}$ is the jth component of the λth irreducible representation of the smaller of the two groups which we designate as G_s. Let T be a symmetry operation of G_s and $\mathbf{K}'=T(\mathbf{K})$ be the unit vector produced from $\mathbf{K}$ by the symmetry operation. Since this new direction is equivalent to the initial one as far as either the complex or the crystal are concerned the following statements may be made: Independent of any model for the phonons, the phonon modes may be separated into the same set of polarizations for the direction of propagation $\mathbf{K}'$ as for $\mathbf{K}$, and these polarizations correspond to the same displacement vectors relative to $\mathbf{K}'$ as the original set did relative to $\mathbf{K}$. It is clear then that the displacements of the components of the complex by the phonon traveling in the direction $\mathbf{K}'$ is the same as the set produced by the phonon traveling in the direction $\mathbf{K}$ and with the corresponding polarization after that set has been transformed by the symmetry operation T. In addition $\rho_p(\mathbf{K},\omega)=\rho_p(\mathbf{K}',\omega)$. Therefore, we may average (17) over the phonons traveling in equivalent directions to obtain

$$[Q_r{}^{(\lambda)},Q_s{}^{(\mu)}]_\omega=\left(\frac{1}{n'}\right)\sum_p\int d\Omega_{\mathbf{K}}\rho_p(\mathbf{K},\omega)\times\sum_T\langle n_{\mathbf{K}p\omega}|TQ_r{}^{(\lambda)}|n_{\mathbf{K}p\omega}+1\rangle\times\langle n_{\mathbf{K}p\omega}+1|[TQ_s{}^{(\mu)}]^\dagger|n_{\mathbf{K}p\omega}\rangle,\quad(18)$$

where n' is the number of symmetry operations in G_s and the sum over T is over all symmetry operations in G_s. It follows from the orthogonality theorem for the representation matrices of T that[11]

$$[Q_r{}^{(\lambda)},Q_s{}^{(\mu)}]_\omega=C^{(\lambda)}(\omega)\delta_{rs}\delta_{\lambda\mu}.\quad(19)$$

If the same representation occurs more than once, the cross products of corresponding elements will not vanish and if $Q_s{}^{(\lambda)\prime}$ is an element of a repeated representation, then we have

$$[Q_r{}^{(\lambda)\prime},Q_s{}^{(\lambda)}]_\omega=B^{(\lambda)}(\omega)\delta_{rs}\quad(20a)$$

and

$$[Q_r{}^{(\lambda)\prime},Q_s{}^{(\lambda)\prime}]_\omega=C^{(\lambda)\prime}(\omega)\delta_{rs},\quad(20b)$$

so that if the irreducible representation is repeated n times there are $n(n+1)/2$ independent constants introduced.

The number of irreducible representations which contribute to the spectral densities defined by (16) depend on the matrix elements of the operators $V_j{}^{(\lambda)}$. These operators transform in the same way as the

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[11] V. Heine, *Group Theory in Quantum Mechanics* (Pergamon Press, New York, 1960), p. 139.

corresponding Q's. There is clearly only one independent constant $V^{(\lambda)}$ for each irreducible representation. The eigenstates of W_I+V_0 consist of degenerate sets which are irreducible representations of the group which characterizes V_0. Since G_s is a subgroup of the group defined by the Hamiltonian, the eigenfunctions of (1) can be written as linear combinations of ionic states which transform as the irreducible representations of G_s.

$$\psi_{hk}=\sum_{j\lambda} A_{hkj\lambda}\psi_j^{(\lambda)} \tag{21}$$

and the matrix elements of V operators are

$$\langle\psi_{h'k'}|V_i^{(\mu)}|\psi_{hk}\rangle=\sum_{\gamma\lambda jl} A_{hkj\lambda}A_{h'k'l\gamma}^*\langle\mu\lambda ij|\mu\lambda\gamma l\rangle V^{(\mu)} \tag{22}$$

in which we have used the generalized Wigner coefficients for irreducible representations.[12] From (21), it is apparent that the number and nature of the irreducible representations which contribute to the direct relaxation processes is governed by the nature of the states and the normal coordinates. Van Vleck[7] has considered the limitations on the number of normal modes for several cases and Orbach[2] has treated others. In general, if the matrix element of $V_j^{(\lambda)}$ does not vanish and the irreducmatrix element of $V_j^{(\lambda)}$ does not vanish and the irreducible representation λ occurs n times, there are $n(n+1)/2$ independent constants introduced into (16) of the form

$$[V^{(\lambda)}]^2C^{(\lambda)}(\omega),\quad V^{(\lambda)}V^{(\lambda)\prime}B^{(\lambda)}(\omega),\ \cdots,\ \text{etc.}$$

3. Calculation of Spin-Lattice Relaxation Rates

A. The Static Spin Hamiltonian

The Hamiltonian (7) when specialized to effective axial symmetry may be written

$$\mathcal{H}_S=\beta g_{\|}H_zS_z+\beta g_{\perp}(H_xS_x+H_yS_y)+AI_zS_z+B(I_xS_x+I_yS_y)+PI_z^2, \tag{23}$$

where the z axis is the symmetry axis of the complex and the x, y axes are any orthogonal pair perpendicular the the symmetry axis. If the magnetic field is the largest term in (23), one should apply perturbation theory in a representation in which the Zeeman interaction is diagonal. This is accomplished by choosing states for which the electronic spin is quantized in the direction $\mathbf{g}\cdot\mathbf{H}$. In the treatment of the hyperfine interaction, the nuclear spin should be quantized in the direction $(\mathbf{g}\cdot\mathbf{H})\cdot\mathbf{A}$ so that the part of the interaction which is diagonal in the electronic spin is also diagonal in the nuclear spin. The direction of these axes relative to the symmetry axis is shown in Fig. 1 for the case in which the magnetic field is in the xz plane and at an angle θ with the z axis. The angles ψ and χ defined in the figure are given by the relations $\tan\psi=(g_{\perp}/g_{\|})\tan\theta$ and $\tan\chi=(B/A)\tan\psi$. In order to obtain the appropriate components when the three vectors **H**, **S**, and **I** are referred to different axes in terms of their values when all of the vectors are referred to the symmetry axis, a mixed coordinate transformation must be made:

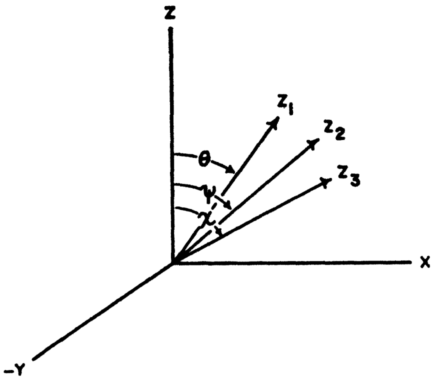

FIG. 1. A diagram of the coordinate axes used in the quantization of the spin Hamiltonian when the g and A tensors are anisotropic. The axis z_1 is in the direction of **H**, the z_2 axis is in the direction of $\mathbf{g}\cdot\mathbf{H}$, and the z_3 axis is in the direction of $(\mathbf{g}\cdot\mathbf{H})\cdot\mathbf{A}$. The angles θ, ψ, and χ are defined here for use in the text.

$$\begin{aligned} g_{ij}(\theta)&=\sum_{kl} R_{ik}(\theta)g_{kl}(R^{-1})_{lj}(\psi),\\ A_{ij}(\theta)&=\sum_{kl} R_{ik}(\chi)A_{kl}(R^{-1})_{lj}(\psi),\\ P_{ij}(\theta)&=\sum_{kl} R_{ik}(\chi)P_{kl}(R^{-1})_{lj}(\chi),\end{aligned} \tag{24}$$

where the matrix $R(\Omega)$ is that for the transformation of a vector by the rotation of the coordinates by the angle Ω about the y axis. The components of the tensors on the right-hand side are referred to the symmetry axis. In writing the Hamiltonian, we omit explicit indication of the dependence on θ and let it be understood that Greek subscripts ξ, η, and ζ refer to the axes defined in Fig. 1 and may be different axes for the nuclear or electron spin operators. The spin Hamiltonian takes the form

$$\begin{aligned}\mathcal{H}_S=G_{\zeta\zeta}S_\zeta+A_{\zeta\zeta}I_\zeta S_\zeta+A_{\zeta+}I_\zeta S_++A_{+\zeta}I_+S_\zeta+A_{-+}I_-S_+\\ +A_{++}I_+S_++P_{\zeta\zeta}I_\zeta^2+P_{\zeta+}(I_\zeta I_++I_+I_\zeta)+P_{+-}I_+I_-\\ +P_{++}I_+I_++\text{Hermitian adjoint},\end{aligned} \tag{25}$$

where

$$G_{\zeta\zeta}=\beta Hg_{\zeta\zeta};\ A_{\zeta+}=\tfrac{1}{2}A_{\zeta\xi};\ A_{+\zeta}=0;\ A_{-+}=\tfrac{1}{4}(A_{\xi\xi}+A_{\eta\eta});$$
$$A_{++}=\tfrac{1}{4}(A_{\xi\xi}-A_{\eta\eta});\quad P_{\zeta+}=\tfrac{1}{2}P_{\zeta\xi};\quad P_{++}=\tfrac{1}{4}P_{\xi\xi}=P_{+-}.$$

The components $A_{\xi\zeta}$, $A_{\xi\eta}$, $A_{\eta\xi}$, $A_{\eta\xi}$, and $A_{\eta\zeta}$ are zero because of the form of the transformation (24). Constant terms in the quadrupole interaction have been omitted. When the transformations (24) are carried out, Eq. (25) gives results which agree with Bleaney.[13]

For our discussion of relaxation processes only the

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[12] J. S. Griffith, *The Theory of Transition Metal Ions* (Cambridge University Press, New York, 1961), p. 168.

[13] B. Bleaney, Phil. Mag. 42, 441 (1951).

first-order expressions for the energy eigenvalues are required:

$$E_{\sigma m}=G_{\zeta\zeta}\sigma+A_{\zeta\zeta}m\sigma+P_{\zeta\zeta}m^2-\tfrac{1}{2}P_{\xi\xi}m^2, \qquad (26)$$

where σ and m are eigenvalues of S_ζ and I_ζ. If we assume that the quadrupole interaction is much smaller than the magnetic hyperfine interaction, we may write the first-order wave function as

$$\langle\psi_{\frac{1}{2},m}|=\langle\tfrac{1}{2},m|+\sum_{\sigma m''}\frac{\langle\frac{1}{2},m|\mathcal{H}'|\sigma,m''\rangle\langle\sigma,m''|}{(E_{-\frac{1}{2},m'}-E_{\sigma,m''})}, \qquad (27a)$$

$$|\psi_{-\frac{1}{2},m'}\rangle=|-\tfrac{1}{2},m'\rangle+\sum_{\sigma m''}\frac{\langle\sigma,m''|\mathcal{H}'|-\frac{1}{2},m'\rangle}{(E_{-\frac{1}{2},m'}-E_{\sigma,m''})}|\sigma,m''\rangle, \qquad (27b)$$

where $\mathcal{H}'$ is the nondiagonal part of $\mathcal{H}_S$.

B. The Matrix Elements of the Spin-Lattice Hamiltonian

We assume that the dynamic tensors have been calculated for the case in which all vectors are referred to the symmetry axes. To calculate matrix elements between the eigenstates of (25), the dynamic tensor components must be transformed by Eqs. (24). The spin lattice Hamiltonian may be written in precisely the same form as (25) except that the parameters are primed. Because there is less symmetry in the dynamic tensors, the expressions for the parameters are more involved when they are expressed in terms of Cartesian components. In the dynamic analog of (25), we have

$$\begin{aligned}
G_{\zeta+}'&=(\beta H/2)(g_{\zeta\xi}'-ig_{\zeta\eta}');\\
A_{\zeta+}'&=\tfrac{1}{2}(A_{\zeta\xi}'-iA_{\zeta\eta}');\\
A_{+\zeta}'&=\tfrac{1}{2}(A_{\xi\zeta}'-iA_{\eta\zeta}');\\
A_{-+}'&=\tfrac{1}{4}(A_{\xi\xi}'+A_{\eta\eta}')+\tfrac{1}{4}i(A_{\xi\eta}'-A_{\eta\xi}');\\
A_{++}&=\tfrac{1}{4}(A_{\xi\xi}'-A_{\eta\eta}')-\tfrac{1}{4}i(A_{\xi\eta}'+A_{\eta\xi}').
\end{aligned} \qquad (28)$$

The components of the P' tensor have the same form as those of A'.

We shall work out the matrix elements of the dynamic spin Hamiltonian between those states for which the energy difference is of the order of $G_{\zeta\zeta}$. The relaxation rates for the other transitions are several orders of magnitude slower because of the ω^2 dependence of the density of phonon states. We find for those matrix elements

$$\langle\psi_{\frac{1}{2},m}|\mathcal{H}_{\mathrm{SL}}|\psi_{-\frac{1}{2},m'}\rangle=\langle\tfrac{1}{2},m|\mathcal{H}_{\mathrm{SL}}|-\tfrac{1}{2},m'\rangle$$
$$=\sum_{m''\sigma}\left\{\frac{\langle\frac{1}{2},m|\mathcal{H}'|\sigma,m''\rangle\langle\sigma,m''|\mathcal{H}_{\mathrm{SL}}|-\frac{1}{2},m'\rangle}{(E_{\frac{1}{2},m}-E_{\sigma,m''})}+\frac{\langle\frac{1}{2},m|\mathcal{H}_{\mathrm{SL}}|\sigma,m''\rangle\langle\sigma,m''|\mathcal{H}'|-\frac{1}{2},m'\rangle}{(E_{-\frac{1}{2},m}-E_{\sigma,m''})}\right\}. \qquad (29)$$

When these are worked out in detail, we obtain

$$\langle\psi_{\frac{1}{2},m}|\mathcal{H}_{\mathrm{SL}}|\psi_{-\frac{1}{2},m}\rangle=G_{\zeta+}'+mA_{\zeta+}'-\frac{mA_{\zeta+}}{G_{\zeta\zeta}}(G_{\zeta\zeta}'+mA_{\zeta\zeta}')-\frac{(A_{+\zeta}'A_{-+}+A_{-\zeta}'A_{++})}{2G_{\zeta\zeta}}[C^2(m)+C^2(m-1)]$$
$$+\frac{(P_{\zeta+}'A_{-+}-P_{\zeta-}'A_{++})}{G_{\zeta\zeta}}[2I(I+1)-6m^2]+\frac{2(A_{-+}'P_{\zeta+}-A_{++}'P_{\zeta-})}{A_{\zeta\zeta}}\{2m[2I(I+1)-2m^2-1]\} \qquad (29a)$$

$$\langle\psi_{\frac{1}{2},m}|\mathcal{H}_{\mathrm{SL}}|\psi_{-\frac{1}{2},m+1}\rangle=C(m)\left\{A_{-+}'-\frac{1}{2G_{\zeta\zeta}}[(2m+1)(A_{\zeta+}A_{-\zeta}'+A_{-+}A_{\zeta\zeta}')+2G_{\zeta\zeta}'A_{-+}]\right.$$
$$+\frac{(2m+1)}{G_{\zeta\zeta}}[A_{-+}P_{\zeta\zeta}'-A_{\zeta+}P_{\zeta-}'+2A_{++}P_{--}'-2A_{-+}P_{-+}']$$
$$\left.-\frac{2}{A_{\zeta\zeta}}[(2m+1)\{(2m+1)A_{\zeta+}'+2G_{\zeta+}'\}P_{\zeta-}+\tfrac{1}{2}\{C^2(m+1)+C^2(m-1)\}P_{--}A_{++}']\right. \qquad (29b)$$

$$\langle\psi_{\frac{1}{2},m}|\mathcal{H}_{\mathrm{SL}}|\psi_{-\frac{1}{2},m+2}\rangle=-C(m)C(m+1)\left\{\frac{1}{G_{\zeta\zeta}}[A_{-\zeta}'A_{-+}+2A_{\zeta+}P_{--}'-2A_{-+}P_{\zeta-}']\right.$$
$$\left.+\frac{2}{A_{\zeta\zeta}}[(2m+3)(2m+1)A_{-+}'P_{\zeta-}+(m+1)A_{\zeta+}'P_{--}]\right. \qquad (29c)$$

where $C^2(m)=I(I+1)-m(m+1)$. The matrix elements $\langle\psi_{\frac{1}{2},m+1}|\mathcal{H}_{\mathrm{SL}}|\psi_{-\frac{1}{2},m}\rangle$ and $\langle\psi_{\frac{1}{2},m+2}|\mathcal{H}_{\mathrm{SL}}|\psi_{-\frac{1}{2},m}\rangle$ can be obtained from (29b) and (29c) by changing the subscripts (+) of the tensors which refer to the nuclear spin to a (−), and changing the sign of all terms which contain elements of either the dynamic or static quadrupole tensors.

It is instructive to note that the terms containing the elements of the static quadrupole tensor have the static hyperfine splitting in the denominator. The static quadrupole terms can therefore lead to important effects even though the terms are too small to produce observable splittings in the paramagnetic resonance spectrum. The dynamic quadrupole terms and dynamic hyperfine terms have coefficients which are comparable and these tensors must be of comparable magnitude in order to compete in the direct relaxation processes.

The calculation of the spin-lattice relaxation rates requires the evaluation of the square of the matrix elements given in (29). For every product of the components of the primed tensors, a spectral density defined by Eq. (16) must be inserted and the entire result multiplied by $1/h$. In part II, a detailed application of these results is made; but for a case in which all of the quadrupole terms are omitted and the static spin Hamiltonian is isotropic.

II. AN APPLICATION

In this part of the paper, the method described above is applied to divalent cobalt ions in the X site of lanthanum zinc double nitrate (La-Zn).[14] The purpose is twofold: to illustrate the development of the spin-lattice Hamiltonian for a relatively complex situation, and to obtain expressions for the relaxation rates with as few undertermined constants as possible. We have chosen divalent cobalt in this particular site because a large amount of experimental data is available for comparison with theoretical results.[15]

The nuclear spin of the 100% abundant isotope Co^{59} is $\frac{7}{2}$ so that there are sixteen hyperfine levels. For the X site of La-Zn, the static spin Hamiltonian constants at 4.2° K are $g_{\|}=4.37$, $g_{\perp}=4.31$, $A=0.00986$ cm^{-1}, and $B=0.00948$ cm^{-1}. No static quadrupole interaction has been detected. The spin Hamiltonian constants imply that the local symmetry is very nearly cubic. The crystal field is presumed to be due to an octahedron of water molecules oriented with the [111] axis along the trigonal axis of the crystal, and it appears that the octahedron is virtually perfect for the X site of La-Zn. For other diamagnetic constituents (La-Mg, Bi-Zn, etc.), the octahedron has an appreciable trigonal distortion. In our treatment we assume that the local symmetry is perfectly cubic, the static spin Hamiltonian is perfectly isotropic, and that quadrupole effects are negligible. In this approximation, we are able to obtain expressions for those relaxation processes in which the energy of the spin system changes by $\sim g\beta H$ in terms of four constants which depend on the phonon spectrum, the sources of the crystal field and the coupling of the phonons to the sources of the field. Since there are 22 relaxation processes that should be competitive and they all depend on the direction of the applied magnetic field relative to the crystal axes, a very complete test of the theory can be made.

1. The Dynamic *g* Tensor

A. Divalent Cobalt in a Cubic Field

The energy levels for divalent cobalt in a cubic field are shown schematically in Fig. 2. When the spin-orbit interaction is ignored, the lowest states of the ^4F term are an orbital triplet, the wave functions of which form a representation $^4T_1$ of the octahedral group. The spin-orbit interaction splits the levels of $^4T_1$ into three Kramers multiplets with the doublet lowest. The approximate separation of the levels are given in Fig. 2.

The theory of the static spin Hamiltonian has been given in great detail by Abragam and Pryce[16] and a simplified but highly instructive discussion has been given by Griffith.[17] A specialized discussion of cubic symmetry is given by Low.[18] Comparison of Fig. 2 with the energy diagram given by Low shows that we have omitted the levels which split off from the ^2G term. Low has discussed the conditions under which this level may affect the calculation of the static spin Hamiltonian. The success of Abragam and Pryce in calculating the spin Hamiltonian parameters for hydrated cobalt complexes suggest that we may ignore these levels as they did.

The wave functions of $^4T_1$ may be written in terms of ionic ^4F wave functions and sorted into the components[7]

$$\phi_z=(\tfrac{1}{3})^{1/2}(\psi_1+\psi_2+\psi_3), \tag{30a}$$

$$\phi_x=(\tfrac{2}{3})^{1/2}[\psi_1-\tfrac{1}{2}(\psi_2+\psi_3)], \tag{30b}$$

$$\phi_y=(\tfrac{1}{2})^{1/2}(\psi_2-\psi_3), \tag{30c}$$

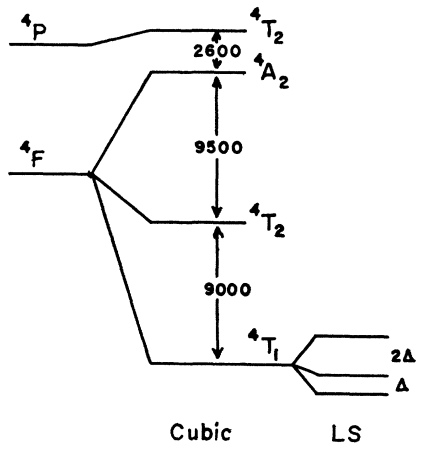

FIG. 2. A schematic diagram of the energy levels for Co^{2+} in a cubic field in units of cm^{-1}. Splittings caused by the spin-orbit interaction are shown at the far right. Several levels which arise from the ionic ^2G level are not shown.

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[14] J. W. Culvahouse, W. Unruh, and R. C. Sapp, Phys. Rev. **121**, 1370 (1961).

[15] W. P. Unruh and J. W. Culvahouse, following paper [Phys. Rev. **129**, 2441 (1963)].

[16] A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A206**, 175 (1951).

[17] See reference 12, p. 304.

[18] W. Low, Phys. Rev. **109**, 256 (1958).

where the functions ψ_1, ψ_2, and ψ_3 are defined on page 78 of Van Vleck's paper. The z axis is the [111] direction of the octahedron which in our case is the trigonal axis of the crystal. These functions have the same transformation properties under the operations of the octahedral group as do real p wave functions. Therefore, the matrix elements of the angular momentum operator $\mathbf{L}$ between the states (30) are proportional to those of an effective operator $\mathbf{l}$ between p states.

$$\langle\phi_i|\mathbf{L}|\phi_j\rangle=\delta\langle p_i|\mathbf{l}|p_j\rangle, \tag{31}$$

where $|p_i\rangle$ is the p state with the same transformation properties under the cubic group as the $|\phi_i\rangle$. For the wave functions given in (30), the value of δ is -1.5. If some of the ^4P term is admixed by the cubic field, the isomorphism still exists but the value of δ is changed and in the limit of a very strong field will approach -1.0. At the end of this section we show that δ is near -1.5 for the present situation. For our calculations, it is desirable to use combinations of the wave functions (30) which are eigenfunctions of l_z:

$$\begin{aligned}|1,\pm 1\rangle&=(1/\sqrt{2})(\phi_x\pm i\phi_y),\\ |1,0\rangle&=i\phi_z.\end{aligned} \tag{32}$$

These wave functions obey the phase convention $(|l,m\rangle)^*=(-1)^{l+m}|l,-m\rangle$, which is convenient for the use of Wigner coefficients in the addition of half-integral angular momentum.[19]

Using the effective angular momentum $\mathbf{l}$, the combined effects of the spin-orbit interaction and a trigonal distortion can be described very compactly with the effective Hamiltonian

$$\mathcal{H}_e=ql_z^2+\delta\lambda(\mathbf{l}\cdot\mathbf{S}_e), \tag{33}$$

where the z axis is the trigonal axis of the crystal, $\mathbf{S}_e$ is the ionic spin and λ is the fine structure constant. In addition there are small effects due to the admixture of the T_2, A_2, and P levels by the spin orbit interaction and the trigonal field. These effects are rather tedious to calculate, but from the work of reference 16, we can be sure that they do not affect the g factors by more than 5%. The difference for $g_{\parallel}$ and $g_{\perp}$ for the X ion of La-Zn, corresponds to a value of $q/\lambda\approx 0.01$. We completely ignore the trigonal splitting and use the effective Hamiltonian

$$\mathcal{H}_e'=\tfrac{1}{2}\delta\lambda[J(J+1)-23/4], \tag{34}$$

where $\mathbf{J}=\mathbf{l}+\mathbf{S}_e$, and $J=5/2$, $3/2$, $1/2$. For the free ion, $\lambda=-180$ cm^{-1} and therefore $\delta\lambda\approx+270$ cm^{-1} which implies that the doublet is lowest. The eigenfunctions of $\mathcal{H}_e'$ are

$$|J,M_J\rangle=\sum_{m_l,m_S}\langle lS_e m_l m_S|lS_eJM_J\rangle|l,m_l\rangle|S_e,m_S\rangle. \tag{35}$$

If the eigenfunctions on the right conform with the phase convention used above, the $|J,M_J\rangle$ does also.[19]

When a magnetic field is applied, the states with $J=1/2$ are mixed with those having larger J values. The admixture of higher lying levels can safely be ignored. Since the magnetic moment operator is a vector operator, only the states with $J=3/2$ will be admixed with the $J=1/2$ states. We obtain for the first-order wave functions in an applied field

$$\begin{aligned}|\pm\rangle=&\;|\tfrac{1}{2},\pm\tfrac{1}{2}\rangle\\ &-\frac{2}{3\delta\lambda}\sum_{M_J}\langle\tfrac{3}{2},M_J|\boldsymbol{\mu}\cdot\mathbf{H}|\tfrac{1}{2},\pm\tfrac{1}{2}\rangle|\tfrac{3}{2},M_J\rangle,\end{aligned} \tag{36}$$

where $\boldsymbol{\mu}=\beta(2\mathbf{S}_e+\delta\mathbf{l})$.

B. The Static and Dynamic g Tensors

The wave functions (36) are used to calculate the static g tensor by defining states $|Sm\rangle$ which are eigenfunctions of the effective spin operators $\mathbf{S}$ and S_z. The g tensor can be deduced by a comparison of the matrix elements of $\boldsymbol{\mu}\cdot\mathbf{H}$ calculated in the space defined by the wave functions $|\pm\rangle$ with the matrix elements of $\mathbf{H}\cdot\mathbf{g}\cdot\mathbf{S}$ calculated in the space spanned by the wave functions $|Sm\rangle$. This comparison yields the result

$$g_0=g_{xx}=g_{yy}=g_{zz}=2\lim_{H\to 0}\left(\frac{\langle+|H_z\mu_z|+\rangle}{H_z}\right)=\frac{2}{3}(5-\delta). \tag{37}$$

The dynamic g tensor is gotten by a comparison of the matrix elements of V' calculated in the space defined by $|\pm\rangle$ with the result for $\mathcal{H}_{\mathrm{SL}}=\mathbf{H}\cdot\mathbf{g}'\cdot\mathbf{S}$ calculated in the space defined by $|Sm\rangle$. In this way we find for the dynamic g tensor relative to the symmetry axes of the crystal

$$g_{zz}'=4\epsilon F_0, \tag{38a}$$

$$g_{xx}'=-2\epsilon F_0+2\sqrt{3}\epsilon\,\mathrm{Re}(F_2), \tag{38b}$$

$$g_{yy}'=-2\epsilon F_0-2\sqrt{3}\epsilon\,\mathrm{Re}(F_2), \tag{38c}$$

$$g_{xz}'=g_{zx}'=4\epsilon\,\mathrm{Re}(F_1), \tag{38d}$$

$$g_{yz}'=g_{zy}'=4\epsilon\,\mathrm{Im}(F_1), \tag{38e}$$

$$g_{xy}'=g_{yx}'=2\sqrt{3}\epsilon\,\mathrm{Im}(F_2), \tag{38f}$$

where $\epsilon=(5^{1/2}/3)(2-\delta)$, and

$$F_0=-\langle\tfrac{3}{2},\tfrac{1}{2}|V'|\tfrac{1}{2},\tfrac{1}{2}\rangle/(\tfrac{3}{2}\lambda\delta), \tag{39a}$$

$$F_1=-\langle\tfrac{3}{2},-\tfrac{1}{2}|V'|\tfrac{1}{2},\tfrac{1}{2}\rangle/(\tfrac{3}{2}\delta\lambda), \tag{39b}$$

$$F_2=-\langle\tfrac{3}{2},-\tfrac{3}{2}|V'|\tfrac{1}{2},\tfrac{1}{2}\rangle/(\tfrac{3}{2}\delta\lambda). \tag{39c}$$

These results have been greatly simplified by the use of the fact that V' is Hermitian and invariant under time reversal.

The dynamic hyperfine interaction tensors could be calculated by a method analogous to that used for the g tensor. In the next section we show that this is not necessary because the hyperfine interaction tensor in

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[19] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1957), p. 51.

this case can be simply related to the g tensor for an arbitrary V'.

Equations (38) can also be used to investigate the validity of our approximation by allowing V' to be a small *static* trigonal distortion. It can be seen by reference to Eq. (33), where the effect of the trigonal distortion has been represented in terms of l_z, that F_1 and F_2 are zero. We therefore find for small trigonal distortions in the present approximation

$$\tfrac{1}{3}(g_{zz}+g_{xx}+g_{yy})=\tfrac{2}{3}(5-\delta)=g_0. \tag{40}$$

Inserting the experimental values for the g tensor of cobalt ions in the X site, we find $\delta=-1.497$. When account is taken of the small effects from admixture of the higher levels by spin-orbit interaction, $\delta=-1.45$ is probably a better choice. We continue to ignore the admixture of higher states and use Eqs. (38) with $\delta=-1.5$, and the slight static trigonal distortion is ignored.

C. Evaluation of the Spectral Densities for the g Tensors

Since we are ignoring the admixture of higher lying levels by the spin-orbit and trigonal distortion, the matrix elements of V' will be evaluated between states for which the orbital parts are components of the representation T_1 of the cubic group. This implies that only those components of V' which transform as the irreducible representations contained in the direct product $T_1 \times T_1$ contribute in first order. This is equivalent to our general prescription given in Eq. (22). This limits the participating normal modes to the gerade vibrational modes of the octahedral complex. We use for these six modes the notation of Van Vleck.[7] In Table I we give the decomposition of these modes into the irreducible representations of O_h and, for latter use, their decomposition for D_3.

The expansion of V' in these normal modes has been given by Van Vleck, and he has worked out the matrix elements for the basis functions of T_1 defined by our Eqs. (30). Changing to the basis defined by (40), we obtain

$$\langle +1|V'|+1\rangle=\langle -1|V'|-1\rangle=-\tfrac{1}{3}\sqrt{3}bQ_4', \tag{41a}$$

$$\begin{aligned}\langle +1|V'|0\rangle=-\langle -1|V'|0\rangle=&-a\sqrt{3}Q_2+(b/\sqrt{6})Q_5'\\&-i[a\sqrt{3}Q_3+(b/\sqrt{6})Q_6'],\end{aligned} \tag{41b}$$

$$\langle 0|V'|0\rangle=\tfrac{2}{3}\sqrt{3}bQ_4', \tag{41c}$$

and the rest are determined by Hermiticity. The quantities a and b are as defined by Van Vleck. He has worked out their values for a number of ionic terms and for both a charge and dipole model for the sources of the crystal field. The number a corresponds to the constant $V^{(\lambda)}$ in equation (22) for $\lambda=E$ and b is the corresponding number for $\lambda=T_2$. Thus if a and b are freely adjusted, the model is just as general as our assumption that the octahedron is the source of the crystal field independent of nature of the individual sources. We are content to carry these constants as parameters which may be compared with Van Vleck's values after they have been adjusted to fit experimental data. This comparison is complicated by the fact that the experimental results determine products of these numbers with spectral densities of the normal modes.

TABLE I. The gerade normal modes of vibration of an octahedron as defined by Van Vleck and their classification by the irreducible representations of O_h and D_3.

O_h	D_3
A_1: Q_1	A_1: Q_1
E: Q_2, Q_3	A_1: Q_4'
T_2: Q_4', Q_5', Q_6'	E: Q_2, Q_3
	E: $-Q_6'$, Q_5'

When the matrix elements (41) are used together with the expansion of the $|JM_J\rangle$ states given by (44), we find

$$F_0=-[bD/(15)^{1/2}]Q_4', \tag{42a}$$

$$\mathrm{Re}(F_1)=+[D/(10)^{1/2}][(b/6)^{1/2}Q_5'-a\sqrt{3}Q_2], \tag{42b}$$

$$\mathrm{Im}(F_1)=-[D/(10)^{1/2}][(b/6)^{1/2}Q_6'+a\sqrt{3}Q_3], \tag{42c}$$

$$\mathrm{Re}(F_2)=-[D/(15)]^{1/2}[(\tfrac{2}{3})^{1/2}bQ_6'-a\sqrt{3}Q_3], \tag{42d}$$

$$\mathrm{Im}(F_2)=+[D/(15)]^{1/2}[(\tfrac{2}{3})^{1/2}bQ_5'+a\sqrt{3}Q_2], \tag{42e}$$

where $D=-(2\epsilon)/3\delta\lambda$.

These values for the F_i when substituted into Eqs. (38) yield an expansion of the dynamic g tensor in terms of the normal modes of the complex which is a realization of Eq. (10). The calculation of the relaxation rates require the evaluation of the spectral densities of the g tensor by means of Eq. (16). Since the rotational symmetry of the double nitrate crystals is only $\bar{3}m(D_3)$,[14] the equivalence and orthogonality of the normal modes when driven by the lattice vibrations will be determined by the number of irreducible representations of D_3 which is the group G_s discussed in part I. The average values of the normal modes as defined by Eq. (17) are such that

$$\begin{aligned}&[Q_2,Q_2]_\omega=[Q_3,Q_3]_\omega=C_2,\\&[Q_4',Q_4']_\omega=C_1,\\&[Q_5',Q_5']_\omega=[Q_6',Q_6']_\omega=C_4,\\&[Q_5',Q_2]_\omega=-[Q_3,Q_6']_\omega=C_3,\end{aligned} \tag{43}$$

and the average of the products of all other pairs of Q's in (42) are zero. If one had cubic symmetry for the crystal, one would have $C_1=C_4$ and $C_3=0$. If one assumes an isotropic phonon spectrum and that the components of the octahedron are free to vibrate just as an atom in a monoatomic crystal, the result given by Van Vleck is obtained: $C_1=C_2=C_4$, and $C_3=0$. It is apparent that the maximum possible value of C_3 is $(C_4C_2)^{1/2}$ which corresponds to a complete equivalence

TABLE II. The spectral densities for the components of the g tensor of divalent cobalt in a nearly cubic site but with a phonon spectrum with only trigonal symmetry.

$$\begin{aligned}
&J_{xx;xx}=J_{yy;yy}=(4\alpha_4+2\alpha_3+\alpha_2+\tfrac{1}{4}\alpha_1)\\
&J_{xx;yy}=-(4\alpha_4+2\alpha_3+\alpha_2-\tfrac{1}{4}\alpha_1)\\
&J_{xy;xy}=(4\alpha_4+2\alpha_3+\alpha_2)\\
&J_{zz;xx}=J_{zz;yy}=-\tfrac{1}{2}J_{zz;zz}=-\tfrac{1}{2}\alpha_1\\
&J_{yz;yz}=J_{xz;xz}=2(\alpha_4-\alpha_3+\alpha_2)\\
&J_{xy;xz}=J_{xx;zy}=-J_{yy;zy}=(\tfrac{3}{2})^{1/2}(2\alpha_4-\alpha_3-\alpha_2)\\
&J_{zz;xy}=J_{zz;zy}=J_{zz;zx}=J_{yy;xz}=J_{xx;xz}=J_{xz;yz}=0\\
&J_{xx;xy}=J_{yy;xy}=J_{yz;xy}=0
\end{aligned}$$

of the two E representations for averaging over the phonon spectrum.

Note added in proof. X-ray measurements reported by David H. Templeton, Allan Zalkin, and J. D. Forester [Bull. Am. Phys. Soc. 7, 608 (1962)] show that the crystal point group is only $\bar{3}$. This does not affect the results obtained here, as the classifications of Q's will be the same as for D_3.

Twenty one of the spectral densities for the g tensors have been tabulated in Table II. The remaining sixty can be derived from the symmetry under interchange of the first and second pair of indices and the interchange of indices within any pair. No superscript is used for the spectral densities in the table as we only use those for the g tensor in expressing relaxation rates. Otherwise the notation is the same as used in part I. The constants used in Table II are defined as

$$\alpha_1=(16/15)D^2b^2C_1,\quad \alpha_2=(12/5)D^2a^2C_2,$$
$$\alpha_3=(4\sqrt{2}/5)D^2abC_3,\quad \alpha_4=(2/15)D^2b^2C_4,\tag{44}$$

where we must have $\alpha_3\leq 2(\alpha_2\alpha_4)^{1/2}$. For cubic symmetry, $\alpha_3=0$, and $\alpha_4=(1/8)\alpha_1$. No more restriction on the α's can be made for an isotropic phonon spectrum.

We have described the spectral densities of the g tensor in terms of four constants. It is apparent that their form depends on the choice of the reference axes. Our choice of the xyz axes is that chosen by Van Vleck because of our choice of basis functions in Eq. (32). The spectral densities can be transformed to another set of axes by the rule for fourth rank Cartesian tensors.

2. The Hyperfine Interaction

Abragam and Pryce[16] in their discussion of the hyperfine interaction have separated the tensor into three parts:

$$\mathbf{A}=\mathbf{A}_L+\mathbf{A}_{Ss}+\mathbf{A}_{Sd}.\tag{45}$$

$\mathbf{A}_L$ is the contribution due to the orbital angular momentum of the $3d$ electrons, $\mathbf{A}_{Ss}$ is the contribution from the admixture of ionic configurations which have unpaired s electrons, and $\mathbf{A}_{Sd}$ arises from the spin moment of the $3d$ electrons. Abragam and Pryce have shown that

$$\begin{aligned}\mathbf{A}_L&=P\mathbf{g}_L,\\ \mathbf{A}_{Ss}&=-\tfrac{1}{2}\kappa P\mathbf{g}_S,\end{aligned}\tag{46a}$$

where P is the hyperfine interaction constant for a d electron. The constant κ is an empirical constant which measures the admixture of configurations with unpaired s electrons. For several hydrated complexes of divalent cobalt, $\kappa=0.325\pm0.01$. The tensors $\mathbf{g}_L$ and $\mathbf{g}_S$ are obtained by the method of the last section by using $\boldsymbol{\mu}_L=\delta\mathbf{l}\beta$ and $\boldsymbol{\mu}_S=2\beta\mathbf{S}_e$. $\mathbf{A}_{Sd}$ depends on the matrix elements of

$$[L(L+1)(\mathbf{I}\cdot\mathbf{S})-\tfrac{3}{2}(\mathbf{L}\cdot\mathbf{S})(\mathbf{L}\cdot\mathbf{I})-\tfrac{3}{2}(\mathbf{L}\cdot\mathbf{I})(\mathbf{L}\cdot\mathbf{S})]$$

and for divalent cobalt in a cubic field, it is not difficult to show that

$$\mathbf{A}_{Sd}=P(2/315)[(12/\delta)-(21\delta/4)]\mathbf{g}_L.\tag{47}$$

For $\delta=-1.5$, we see that $\mathbf{A}_{Sd}$ is clearly negligible, and we subsequently ignore it.

Using the wave functions (35) and the magnetic moment operator $\boldsymbol{\mu}_L$, we find

$$(g_{zz})_L=(g_{xx})_L=(g_{yy})_L=-\tfrac{2}{3}\delta,\tag{48a}$$

and using $\boldsymbol{\mu}_S$, we find

$$(g_{zz})_S=(g_{xx})_S=(g_{yy})_S=10/3.\tag{48b}$$

On the other hand, all of the changes in g due to V' may be written in the form

$$(\Delta g_{ij})_L=-\delta e_{ij},\tag{49a}$$

$$(\Delta g_{ij})_S=2e_{ij}.\tag{49b}$$

This result can be seen by inspection of Eqs. (38) in which all of the changes in $\mathbf{g}$ are proportional to $(5^{1/2}/3)(2-\delta)$ and it is obvious that the first term in the bracket corresponds to the contribution of $\boldsymbol{\mu}_S$ and the second to that of $\boldsymbol{\mu}_L$. In the changes of the g tensor by V', the fraction of the spin contribution is smaller than it is for the cubic field values. Using these results, we may write

$$(\Delta A_{ij})_{L\mp S}/A_0=\Gamma(\Delta g_{ij})_{L+S}/g_0,\tag{50}$$

where

$$\Gamma=\frac{(\kappa+\delta)(5-\delta)}{(\frac{5}{2}\kappa+\delta)(2-\delta)}.\tag{51}$$

For $\delta=-1.5$ and $\kappa=0.325$, we find $\Gamma=3.25$.

The relation (50) should be valid for either the dynamic perturbations described by V' or static perturbations. The available data on the g and A tensors in crystals with a range of slight trigonal distortions give a check on the validity of Eq. (50). The X ion in (La-Mg)·(H_2O), (La-Zn)·(D_2O), and (La-Zn)·(H_2O) provide appropriate data.[20] For all of

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[20] The D_2O in brackets indicates that most of the water of hydration is heavy water.

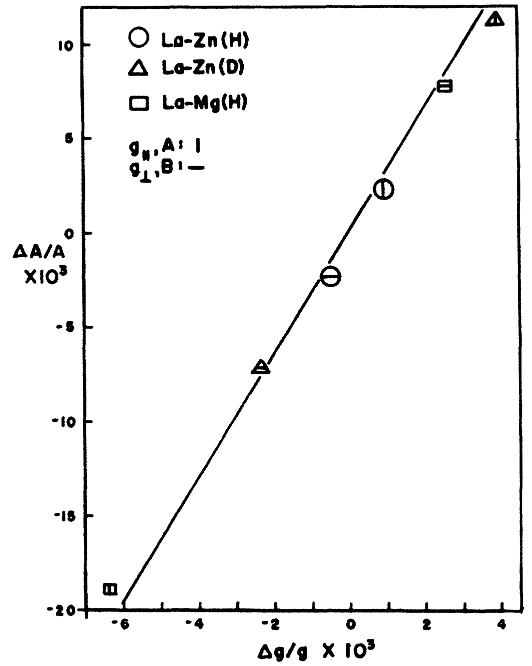

FIG. 3. A plot of the fractional deviation of $g_{\|}$ and $g_{\perp}$ from the weak cubic field values g_0, vs the corresponding deviations of A and B from the weak cubic field values A_0 for a number of double nitrate crystals. The line is drawn in accordance with the theory of part II, Sec. 2 with $\Gamma=3.25$. The experimental errors are represented by the size of the data points.

them $(g_{\|}+2g_{\perp})/3\approx 4.33=g_0$ and $(A+2B)/3\approx 0.0096$ cm$^{-1}=A_0$. In Fig. 3, we have plotted $(g_0-g_{\perp})/g_0$ vs $(A_0-B)/A_0$ and $(g_{\|}-g_0)/g_0$ vs $(A-A_0)/A_0$ for these three salts. The straight line is drawn for $\Gamma=3.25$; a slightly better fit is obtained with $\Gamma=3.0$. The experimental errors for the data in Fig. 3 is represented by the size of the data points, and one could regard these results as a good determination of the constant κ. Data which we have for other diamagnetic constituents agrees with the data plotted, but is less precise.

For the dynamic A tensor we may write

$$A_{ij}'=\beta H(A_0/g_0\beta H)\Gamma g_{ij}'=\Lambda\beta H g_{ij}'=\Lambda G_{ij}'. \quad (52)$$

It follows that the spectral densities for the products of the components of $\mathbf{A}'$ and $\mathbf{G}'$ may be written

$$J_{ij;lm}{}^{(GA)}(\omega)=\Lambda J_{ij;lm}{}^{(GG)}(\omega), \quad (53a)$$

$$J_{ij;lm}{}^{(AA)}(\omega)=\Lambda^2 J_{ij;lm}{}^{(GG)}(\omega), \quad (53b)$$

where

$$J_{ij;lm}{}^{(GG)}(\omega)=\beta^2H^2 J_{ij;lm}{}^{(gg)}(\omega).$$

3. Spin-Lattice Relaxation Rates

The matrix elements of the spin Hamiltonian between the levels of the strong field hyperfine structure of the Kramers doublet are given in Eqs. (29). In the present case, the isotropy of the static spin Hamiltonian permits one to write for any applied magnetic field direction

$$A_{\zeta+}=A_{++}=0,\quad A_{-+}=A_0/2,\quad G_{\zeta\zeta}=G_0=\beta H g_0.$$

We assume that all of the quadrupole effects are negligible and utilize our results for the proportionality of the dynamic A and g tensors. We find

$$\langle\psi_{\frac{1}{2},m}|\mathcal{H}_{\mathrm{SL}}|\psi_{-\frac{1}{2},m}\rangle=\tfrac{1}{2}F(m)(G_{\zeta\xi}'-iG_{\zeta\eta}'), \quad (54a)$$

$$\langle\psi_{\frac{1}{2},m}|\mathcal{H}_{\mathrm{SL}}|\psi_{-\frac{1}{2},m+1}\rangle=\tfrac{1}{4}C(m)\Lambda\{G_{\xi\xi}'+G_{\eta\eta}' -[2-\Lambda(2m+1)]G_{\zeta\zeta}'/\Gamma\}, \quad (54b)$$

$$\langle\psi_{\frac{1}{2},m+1}|\mathcal{H}_{\mathrm{SL}}|\psi_{-\frac{1}{2},m}\rangle=\tfrac{1}{4}C(m)\Lambda(G_{\xi\xi}'-G_{\eta\eta}'+2iG_{\xi\eta}'), \quad (54c)$$

$$\langle\psi_{\frac{1}{2},m+2}|\mathcal{H}_{\mathrm{SL}}|\psi_{-\frac{1}{2},m}\rangle=\langle\psi_{\frac{1}{2},m-2}|\mathcal{H}_{\mathrm{SL}}|\psi_{-\frac{1}{2},m}\rangle\approx\Lambda^2, \quad (54d)$$

where

$$F(m)=\{1+\Lambda m-(\Lambda^2/2\Gamma)[I(I+1)-m^2]\}.$$

The axes $\xi\eta\zeta$ have been defined in part I. In the present case, $\theta=\psi=\chi$, and these axes are the same for all indices and are simply a coordinate system for which the ζ axis is at an angle θ with the z axis and out of the xz plane by an angle ϕ. The relaxation rates calculated from Eq. (13) are

$$W_{m\to m}{}^{-}=\tfrac{1}{4}\mathcal{W}F^2(m)(J_{\zeta\xi;\zeta\xi}+J_{\zeta\eta;\zeta\eta}), \quad (55a)$$

$$W_{m\to m+1}{}^{-}=\tfrac{1}{16}\mathcal{W}\Lambda^2C^2(m)[J_{\xi\xi;\xi\xi}+J_{\eta\eta;\eta\eta}+2J_{\xi\xi;\eta\eta} -2f(m)(J_{\zeta\zeta;\eta\eta}+J_{\zeta\zeta;\xi\xi})+f^2(m)J_{\zeta\zeta;\zeta\zeta}], \quad (55b)$$

$$W_{m+1\to m}{}^{-}=\tfrac{1}{16}\mathcal{W}\Lambda^2C^2(m)(J_{\xi\xi;\xi\xi}+J_{\eta\eta;\eta\eta} -2J_{\xi\xi;\eta\eta}+4J_{\xi\eta;\xi\eta}), \quad (55c)$$

where $\mathcal{W}=(1/h)H^2\beta^2$ and $f(m)=(1/\Gamma)[2+\Lambda(2m+1)]$. In this notation for the relaxation rates, the minus superscript indicates that the ζ component of the electron spin changes by -1. The notations for the inverse transitions are

$$W_{m\to m}{}^{+}=\alpha W_{m\to m}{}^{-},$$

$$W_{m+1\to m}{}^{+}=\alpha W_{m\to m+1}{}^{-},$$

$$W_{m\to m+1}{}^{+}=\alpha W_{m+1\to m}{}^{-},$$

in which α is the Boltzmann factor. In the approximation in which the hyperfine correction to the energy splittings is ignored, it is simply $\exp(-G_0/kT)$ where T is the lattice temperature.

The spectral densities used in Eqs. (55) must be expressed in terms of those in Table II by means of a coordinate transformation. When this transformation is carried out, we obtain for H at an angle θ with the z axis and out of the xz plane by the angle ϕ:

$$W_{m\to m}{}^{-}=\tfrac{1}{4}\mathcal{W}F^2(m)\{(9/4)\alpha_1\sin^2\theta\cos^2\theta +(4\alpha_4+2\alpha_3+\alpha_2)\sin^2\theta(1+\cos^2\theta) +2(\alpha_4-\alpha_3+\alpha_2)[(\cos^2\theta-\sin^2\theta)^2+\cos^2\theta] +(2\alpha_4-\alpha_3-\alpha_2)(4\sin^3\theta\cos\theta)\sin3\phi\}. \quad (56)$$

We do not take the space to write out the angular dependence of the other processes, but use them as well as Eq. (56) in the analysis of experimental data in the following paper. As a check on the work, it is reassuring that the ϕ dependence of (56) has a periodicity of $2\pi/3$ which was put in indirectly by the requirements on the mean-square amplitudes of the normal modes.

III. DISCUSSION

The application of the theory in part II is rather specialized and the major stimulus for it was the experimental results obtained for the Overhauser and Jeffries effects[6] (nuclear orientation produced by saturation of allowed or forbidden transitions of the hyperfine structure) for this ion which are discussed in the next paper. Aside from this, we feel that an exhaustive study of a particular case is a useful preliminary to the development of more general results. It is apparent that general statements concerning relaxation in the hyperfine structure are particularly difficult to make. Without a detailed model of the crystal-field sources and their thermal motion, there is no way to know which of the transition rates $W_{m+1\rightarrow m}^{+}$ or $W_{m\rightarrow m+1}^{+}$ will dominate so to allow the development of the nuclear orientation by the Overhauser process. We may even have $W_{m\rightarrow m+1}^{+}\approx W_{m+1\rightarrow m}^{+}\gg W_{m\rightarrow m}^{+}$ which will cause a Jeffries-type nuclear orientation to fail.

It is apparent that in cases where the hyperfine interaction is sensitive to the crystal field perturbations, the hyperfine effects may compete with the effects from the modulation of the g tensor even in what is usually regarded as a strong field. The hyperfine interaction is sure to be the dominant effect in many Kramers ions at sufficiently low field and the field dependence of the over-all relaxation rate of the system such as might be measured in a concentrated salt would be complicated by the hyperfine relaxation process. It should be possible in many cases to estimate the relative effectiveness of the modulation of the g and A tensors from the change in the static values in environments with different crystal fields. The statement that the corresponding elements of the dynamic g and A tensors are proportional must be justified by a complete analysis such as was made in part II.

No attempt has been made to treat any relaxation processes other than the direct process. It is apparent that when a resolved hyperfine interaction is present, the complications of the direct processes alone offer a considerable challenge; particularly, if (as may happen) almost all of the processes are of comparable strength. For the ions of the iron group, there should exist a temperature below which the Raman and Orbach processes are negligible, and (at least for highly dilute salts) a lower temperature above which the phonon bottleneck is not serious. There is always the possibility noted by Van Vleck[21] that some sort of defect levels are present in the crystal that are near the ground state of the paramagnetic ion and which will serve as relaxation centers. This complication is effectively eliminated by the use of very low concentrations. Low concentrations are also essential in order to eliminate the cross-relaxation process discovered by Bloembergen.[22] We have neglected the possible effects of local modes which arise from the fact that the paramagnetic ion represents an impurity in a lattice of diamagnetic ions. It is easy to find salts for which the mass defect is very slight, but the paramagnetic ion may have a considerably different ionic radius than the diamagnetic ion and produce a local strain field. It appears from the work of Klemens[23] that local-mode effects are important only at relatively high temperatures.

The definition of the static and dynamic spin Hamiltonian in part I is quite general and therefore the description of the direct spin-lattice relaxation in terms of the spectral densities of the dynamic spin Hamiltonian should apply to a wide variety of problems. It is apparent that the introduction of the dynamic spin Hamiltonian does not save any computational labor, nor does it circumvent the problem of the validity of the crystal-field view. It does permit one to easily find the correct states between which one wishes to calculate transition rates for any direction of the applied field. It also permits one to isolate properties of the ion and the symmetry of the environment from other problems in much the same way that the static spin Hamiltonian isolates those properties in the description of the energy levels.

One may take the view that the spectral density tensors are constants to be determined by the experimental measurement of direct spin-lattice relaxation rates just as the parameters of the static spin Hamiltonian are to be determined by experimental measurement of the energy levels. Just as the number of parameters in the static spin Hamiltonian are limited by symmetry considerations, so are those in the dynamic spin Hamiltonian. The spectral densities dealt with in the present paper are fourth rank Cartesian tensors and are always symmetric in the interchange of the first and second pair of indices. Therefore, the number of independent components consistent with a symmetry group G is the same as the number for the piezo-optical tensor.[24] The possibility of considerable angular dependence for the relaxation rates even in cases where the symmetry is high, as indicated by Eq. (56), suggests that a complete definition of the spectral density tensors may be possible. This is particularly likely when the spectral densities for different combinations of the parameters may be related by the properties of the ion alone as was possible for divalent cobalt.

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