

Electron-Paramagnetic-Resonance Line Shape of Ni²⁺ in MgO*

STEPHEN R. P. SMITH†, FRICIS DRAVNIKIS, AND JOHN E. WERTZ

University of Minnesota, Minneapolis, Minnesota 55455

(Received 16 August 1968)

The derivative EPR line shape of Ni²⁺ in MgO ($S=1$) consists of (a) a broad line due to the $\Delta M_s=1$ transitions, which are inhomogeneously broadened by strains, (b) a sharp $\Delta M_s=2$ double-quantum transition, and (c) a line of inverse phase, both situated at the center of the $\Delta M_s=1$ line. This last line is attributed to an "internal cross-relaxation" mechanism which causes a broadening of the $M_s=0 \rightleftharpoons -1$ and $M_s=1 \rightleftharpoons 0$ transitions at a particular site when the strain at that site is sufficiently small to allow overlapping of the two transitions. An expression for the over-all line shape is obtained, using a density-matrix approach for the $S=1$ system, and good agreement with experiment is obtained. Values are obtained for the spin-lattice relaxation parameters by fitting the observed line shape to that predicted by the theory as a function of the microwave power.

I. INTRODUCTION

THE configuration of the Ni²⁺ ion is 3d⁸, and the ground term in an octahedral field is the orbital singlet ${}^3A_2(t_{2g}^6e_g^2)$; thus, a suitable spin Hamiltonian is

$$\mathcal{H} = g\beta\mathbf{H} \cdot \mathbf{S},$$

where $S=1$. The g value for Ni²⁺ in MgO is 2.2145,¹ the deviation from the spin-only value $g=2.0023$ being due principally to the admixture of the term ${}^3T_2(t_{2g}^5e_g^3)$ through the spin-orbit coupling. Therefore, the expected EPR spectrum of Ni²⁺ in MgO is a single line at a magnetic field $H_0 = h\nu/g\beta$, where the two transitions $M_s=1 \rightleftharpoons 0$ and $M_s=0 \rightleftharpoons -1$ are coincident.

However, the observed EPR spectrum is more complicated, as was shown by Orton *et al.*,¹ and, under suitable conditions, up to three lines can be observed in the derivative of the EPR absorption spectrum, all centered at the field H_0 , but having different widths and intensities. (A typical spectrum is shown in Fig. 1.) We shall discuss these three lines in turn:

(a) The normal (NO) line. The principal feature of the spectrum is the broad (at least 40G wide) line which is attributed to the inhomogeneously broadened transitions $M_s=1 \rightleftharpoons 0$ and $M_s=0 \rightleftharpoons -1$. This broadening is caused by random strains in the crystal, and we can make allowance for such strains in the spin-Hamiltonian by adding the first order correction term

$$\epsilon(S_z^2 - \frac{2}{3})$$

to the zeroth-order spin Hamiltonian $\mathcal{H} = g\beta H S_z$. (A discussion of the spin Hamiltonian in the presence of strains is given in the Appendix.) The value of the strain parameter ϵ is different at different Ni²⁺ sites, and a probability function $f(\epsilon)$ can be defined such that $f(\epsilon)d\epsilon$ is the probability that the strain parameter has a value between ϵ and $\epsilon+d\epsilon$ at a given site. Therefore, for a particular value of ϵ , the transitions $M_s=1 \rightleftharpoons 0$ and $M_s=0 \rightleftharpoons -1$ will occur at the fields $H = H_0 - \epsilon/g\beta$ and $H = H_0 + \epsilon/g\beta$, respectively; on averaging over all values of ϵ , weighted by the probability $f(\epsilon)$, a broad line centered at the field H_0 is obtained. The width of the line depends on $f(\epsilon)$, and appears to vary somewhat with different samples, indicating that the samples have varying densities of strains. This broad line is called the NO line.

(b) The double-quantum (DQ) line. A sharp line, roughly 2 G wide, is observed at the center of the NO line, and is attributed to the transition $M_s=1 \rightleftharpoons -1$ with the simultaneous absorption of two microwave quanta. That this is a true DQ line is verified by two facts as demonstrated by Orton *et al.*: first, its intensity varies roughly as the square of the microwave power, and secondly, when subjected simultaneously to two microwave frequencies ν_1 and ν_2 , sharp lines are observed at the three fields given by $2g\beta H = 2\nu_1$, $(\nu_1 + \nu_2)$ and $2\nu_2$. It should be noted that the strain term $\epsilon(S_z^2 - \frac{2}{3})$ influences the energies of the states $|M_s=1\rangle$ and $|M_s=-1\rangle$ to equal extents, so that the width of the

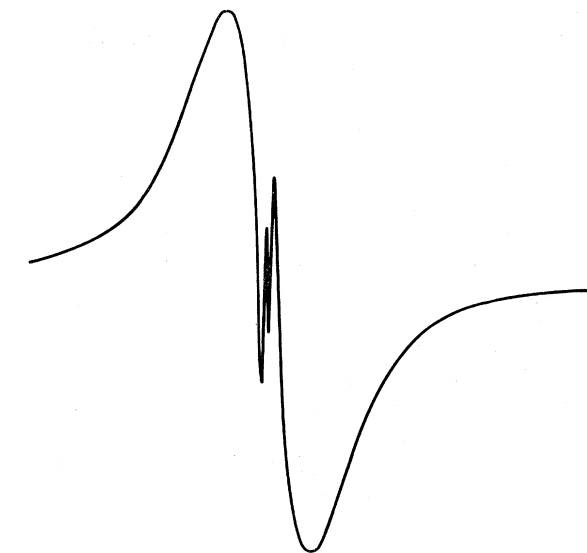


FIG. 1. Typical EPR derivative absorption spectrum, showing the broad NO line, the narrow DQ line at the center, and the IN line of inverse phase and width about twice that of the DQ line.

* Research supported by the U. S. Air Force Office of Scientific Research under Grant No. AFOSR 200-66.

† Present address: Scientific Laboratory, Ford Motor Company, Dearborn, Mich.

¹J. W. Orton, P. Auzins, and J. E. Wertz, Phys. Rev. Letters 4, 128 (1960).

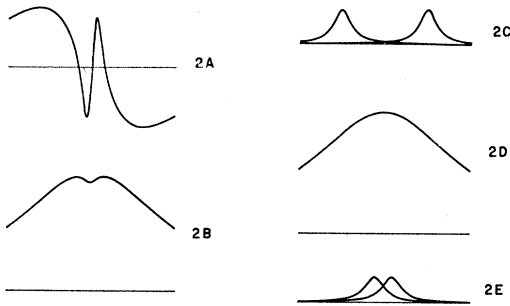


FIG. 2. (A) Diagrammatic derivative curve, showing NO and IN lines; (B) absorption curve for NO and IN lines (integral of curve A); (C) spin packets, corresponding to the transitions $M_s=1 \rightleftharpoons 0$ and $0 \rightleftharpoons -1$; (D) typical strain distribution function $f(\epsilon)$; and (E) spin packets for small strain, broadened by internal cross relaxation.

DQ line is unaffected (to first order in perturbation theory) by the local strains; consequently, the DQ line is much more narrow than the NO line.

(c) The inverse (IN) line. The third line is centered at the same field as the NO and DQ lines, and has a width roughly twice that of the DQ line. It is characterized by the fact that it has a phase which is the inverse of that of the NO and DQ lines in the derivative of the EPR absorption spectrum. This IN line is visible at very low microwave power, when the DQ line has vanished; at higher power, the DQ line grows, and "buries" the IN line.

In this paper, we are primarily concerned with accounting for the existence of the IN line; we show, in Sec. II, that it is caused by a form of cross relaxation between the individual spin packets of the NO line. In Sec. III, a theoretical expression for the over-all line shape is obtained, using the density matrix for an inhomogeneously broadened $S=1$ system; in Sec. IV the theory is compared with the experimental results, and values for the relaxation times are obtained.

II. ORIGIN OF THE IN LINE

Since the IN line persists at vanishingly small microwave powers, it is obviously not connected with any sort of saturation effect; rather, the IN line appears to be a property of an inhomogeneously broadened $S=1$ system, since it is also observed in each of the hyperfine lines of the isoelectronic Co^+ ion in MgO .² Therefore, we shall at present consider the situation at low powers, when the DQ line is not visible. The derivative line shape is as shown in Fig. 2A, where only the NO and IN lines are seen. The corresponding integrated absorption curve is shown in Fig. 2B; it is apparent from this that the IN line is not a true EPR absorption line, but

represents a dip in the intensity of the absorption corresponding to the $M_s=1 \rightleftharpoons 0$ and $0 \rightleftharpoons -1$ transitions.

The broad line is composed of spin packets whose individual width is $1/T_2$, and which occur in pairs symmetrically disposed at a distance ϵ from the center of the line, corresponding to the $M_s=1 \rightleftharpoons 0$ and $0 \rightleftharpoons -1$ transitions for a site with strain ϵ . Two such spin packets are shown in Fig. 2C. In order to obtain the over-all line shape, an average is taken over all values of ϵ using a distribution function $f(\epsilon)$, as discussed in Sec. I. A general form for the function $f(\epsilon)$ may be obtained by arguments similar to those of Grant and Strandberg³ and of Stoneham,⁴ which indicate that the distribution function is somewhere between the limiting cases of Gaussian, i.e.,

$$f(\epsilon) = \frac{1}{W\sqrt{\pi}} \exp\left(-\frac{\epsilon^2}{W^2}\right) \quad (1)$$

and Lorentzian, i.e.,

$$f(\epsilon) = \frac{W}{\pi} \frac{1}{W^2 + \epsilon^2}. \quad (2)$$

Mims and Gillen⁵ have considered the case where the deviations from cubic symmetry at a given site are produced by the electric fields of point charges distributed randomly through the crystal; they express $f(\epsilon)$ in the form

$$f(\epsilon) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\rho e^{-i\rho\epsilon} \exp(-c\rho^{3/2}), \quad (3)$$

where c is a constant proportional to the density of the defects. This expression, which is the Fourier transform (FT) of $\exp(-|\kappa|^{3/2})$, is between the Gaussian [FT of $\exp(-\kappa^2)$] and Lorentzian [FT of $\exp(-|\kappa|)$] expressions, and would seem to be applicable to the case of Ni^{2+} in MgO , since inspection of the wings of the NO line indicates a line shape between Gaussian and Lorentzian.

However, as Mims and Gillen point out, there is no significant difference between the three forms of $f(\epsilon)$ [Eqs. (1)–(3)] so long as one considers the regions between the turning points of the derivative. In particular, all three functions have a maximum for $\epsilon=0$, a typical plot of $f(\epsilon)$ being given in Fig. 2D.

Thus if spin packets of the type shown in Fig. 2C are averaged over ϵ using a distribution function of the type shown in Fig. 2D, the resulting curve will have a shape similar to that of Fig. 2D, without the dip associated with the IN line. Nevertheless, the dip could arise if the most probable value of $|\epsilon|$ were nonzero; in order to bring this about, it might be thought possible to invoke the dynamic Jahn-Teller effect. However, Van Eekelen

² J. W. Orton, P. Auzins, and J. E. Wertz, *Phys. Rev.* **119**, 1691 (1960). The IN line has also been observed for Ni^{2+} in SrTiO_3 by R. S. Rubins and W. Low, in *Paramagnetic Resonance*, edited by W. Low (Academic Press Inc., New York, 1963), Vol. 1, p. 59, and for Ni^{2+} in CaO by W. Low and R. S. Rubins, *ibid.*, p. 79.

³ W. J. C. Grant and M. W. P. Strandberg, *Phys. Rev.* **135**, A715 (1964).

⁴ A. M. Stoneham, *Proc. Phys. Soc. (London)* **89**, 909 (1966).

⁵ W. B. Mims and R. Gillen, *Phys. Rev.* **148**, 438 (1966).

and Stevens⁶ and Böttger⁷ have investigated the dynamic Jahn-Teller effect for an $S=1$ system in an octahedral environment, and did not find that there is, on average, a splitting between the $M_s=1 \rightleftharpoons 0$ and $0 \rightleftharpoons -1$ transitions. In fact, it appears that no reasonable adjustment of the form of $f(\epsilon)$ will account for the occurrence of the IN line, and so we propose the following explanation.

For large values of ϵ , the spin packets are as shown in Fig. 2C, but when ϵ is of the order of the linewidth of the packets ($\sim 1/T_2$), the two packets for a given ϵ will overlap, and a form of cross relaxation can occur between the two transitions $M_s=1 \rightleftharpoons 0$ and $0 \rightleftharpoons -1$. This will have the effect of broadening the spin packets at the center of the line, and so the absorption height of spin packets is less at the center—compare Figs. 2C and 2E. In other words, the effect of the interaction between the two $\Delta M_s=1$ lines is to push intensity away from the center of the line, where the spin packets are overlapping, with the result that the over-all absorption curve has the shape of Fig. 2B. Thus, the resulting IN line in the derivative curve (Fig. 2A) will have a width of the order of the width of the individual spin packets, and a height which depends on the strength of the mechanism responsible for the relaxation between the $\Delta M_s=1$ lines.

In order to express this situation quantitatively, we have used a density-matrix approach in Sec. III, and show that the effect arises very naturally on writing down the equations of motion of the density matrix. The method introduces the various relaxation times parametrically, and is independent of the mechanism giving rise to the relaxation, but in Sec. III B we derive relations between the relaxation parameters, assuming only spin-lattice relaxation. We then derive an expression for the line shape, and show that the parameters obtained by fitting the line shape with experiment are consistent with the assumption of Sec. III B (see Sec. IV).

III. THEORY OF LINE SHAPE

A. Equations of Motion of Density Matrix

The most straightforward approach to the problem of line shapes of magnetic resonance lines is through the semiempirical Bloch equations; relaxation times T_1 and T_2 are defined for the rate at which the longitudinal and transverse components of the magnetization vector \mathbf{M} approach equilibrium after the application of some perturbation, and the shape of the absorption and dispersion signals follow in a straightforward fashion. (See,

for example, Abragam⁸ or Slichter.⁹) In general, however, for a system with more than two levels (i.e., $S > \frac{1}{2}$), more than two relaxation times can be defined, and more than one resonance line is observed; therefore, the Bloch equations are not directly applicable to systems of $S > \frac{1}{2}$ (unless the levels are equally spaced). The most convenient approach for more than two level systems is through the density matrix, and we have used this approach.

The first treatment of magnetic relaxation using the density-matrix formalism was given by Wangsness and Bloch.^{10,11} The present work is based on the theory of Redfield,¹² as presented by Slichter⁹ and by Redfield.¹³ The formalism provides a basis for the calculation of relaxation times, and we shall use this in order to derive relations between the various relaxation parameters that are involved in the description of the line shape; however, we shall not attempt to calculate the relaxation times from first principles.

In order to set down the equations of motion of the density matrix, following Refs. 9 and 13, we shall consider an ensemble of systems each with a Hamiltonian

$$\mathcal{H} = \mathcal{H}_0 + \hbar h_i(t). \quad (4)$$

\mathcal{H}_0 is time-independent, and is the same for all members of the ensemble; its eigenfunctions are denoted by ψ_α , with corresponding eigenvalues $\hbar\omega_\alpha$. The operator $h_i(t)$ is an Hermitian perturbation which is random in time, and is responsible for the relaxation; it is assumed to be different for the different members of the ensemble. Thus, the wave function for each member of the ensemble can be written

$$\Psi = \sum_{\alpha} c_{\alpha}(t) \psi_{\alpha},$$

and the density matrix of the ensemble is defined as

$$\rho_{\alpha\alpha'} = \langle c_{\alpha} c_{\alpha'}^* \rangle, \quad (5)$$

where the angular brackets denote an average over the ensemble, and the asterisk denotes complex conjugate. Therefore, the (ensemble) average of any physical operator A is given by

$$\langle A \rangle = \text{Tr} \rho A. \quad (6)$$

The equation of motion of the $\alpha\alpha'$ component of the density matrix can be written in the form

$$\frac{d\rho_{\alpha\alpha'}}{dt} = -\frac{i}{\hbar} [\mathcal{H}_0, \rho]_{\alpha\alpha'} + \sum_{\beta\beta'} R_{\alpha\alpha'\beta\beta'} [\rho_{\beta\beta'} - \rho_{\beta\beta'}(T)], \quad (7)$$

where the first term represents the usual time variation

⁸ A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, Oxford, England, 1961).

⁹ C. P. Slichter, *Principles of Magnetic Resonance* (Harper & Row, New York, 1964).

¹⁰ R. K. Wangsness and F. Bloch, *Phys. Rev.* **89**, 728 (1953).

¹¹ F. Bloch, *Phys. Rev.* **102**, 104 (1956); **105**, 1206 (1957).

¹² A. G. Redfield, *IBM J. Res. Develop.* **1**, 19 (1957).

¹³ A. G. Redfield, in *Advances in Magnetic Resonance*, edited by J. S. Waugh (Academic Press Inc., New York, 1965), Vol. 1, p. 1.

⁶ H. A. M. Van Eekelen and K. W. H. Stevens, *Proc. Phys. Soc. (London)* **90**, 199 (1967).

⁷ H. Böttger, *Phys. Status Solidi* **23**, 325 (1967); **24**, 65 (1967). In the latter reference, a splitting of the ESR line is obtained, but this splitting appears to vanish due to symmetry arguments of the type discussed in Ref. 6.

in Ψ due to the static Hamiltonian \mathcal{H}_0 , and the second term represents the relaxation effects. $\rho_{\beta\beta'}(T)$ is the value of $\rho_{\beta\beta'}$ when equilibrium is reached between the ensemble and a bath at temperature T ; at equilibrium, only the diagonal elements of the density matrix have nonvanishing values, so that

$$\rho_{\beta\beta'} = \delta_{\beta\beta'} \exp\left(\frac{-\hbar\omega_\beta}{kT}\right) / \sum_{\beta''} \exp\left(\frac{-\hbar\omega_{\beta''}}{kT}\right). \quad (8)$$

The relaxation parameters $R_{\alpha\alpha'\beta\beta'}$ are derived on the basis that the interaction $\hbar h_i(t)$ represents a small perturbation on \mathcal{H}_0 ; they can be related to the matrix elements of $h_i(t)$ by the following expression:

$$R_{\alpha\alpha'\beta\beta'} = J_{\alpha\beta\alpha'\beta'}(\omega_{\beta'} - \omega_{\alpha'}) + J_{\alpha\beta\alpha'\beta'}(\omega_\alpha - \omega_\beta) - \delta_{\alpha'\beta'} \sum_{\gamma} J_{\gamma\beta\gamma\alpha}(\omega_\gamma - \omega_\alpha) - \delta_{\alpha\beta} \sum_{\gamma} J_{\gamma\alpha'\gamma\beta'}(\omega_{\alpha'} - \omega_\gamma), \quad (9)$$

where

$$J_{\alpha\alpha'\beta\beta'}(\omega) = \int_0^\infty \langle \langle \psi_\alpha | h_i(t) | \psi_{\alpha'} \rangle \langle \psi_{\beta'} | h_i(t-\tau) | \psi_\beta \rangle \rangle e^{i\omega\tau} d\tau.$$

The assumptions involved in deriving Eq. (9) are discussed in detail in the sources quoted; we shall simply assume here that the theory is valid in the context to which we wish to apply it.

The static Hamiltonian for the $\text{Ni}^{2+}:\text{MgO}$ system is taken as

$$\mathcal{H}_0 = g\beta H S_z + \epsilon(S_z^2 - \frac{2}{3}), \quad (10)$$

where the effect of local strains is represented by the diagonal term in ϵ , off-diagonal terms being neglected. Thus the eigenfunctions $|M_s\rangle$ of the z component of spin S_z , where $M_s = 1, 0$ and -1 , are also eigenfunctions of \mathcal{H}_0 . However, in a magnetic resonance experiment, a time-varying microwave field is applied perpendicular to the z axis, and we represent the field by

$$\mathcal{H}_1(t) = 2\hbar h S_x \cos\omega t,$$

the total Hamiltonian now being

$$\mathcal{H}_0 = \mathcal{H}_0 + \mathcal{H}_1(t) = \hbar[\omega_0 S_z + e(S_z^2 - \frac{2}{3}) + 2h S_x \cos\omega t], \quad (11)$$

where $\hbar\omega_0 = g\beta H$, and $\hbar e = \epsilon$.

In order to remove the time variation from \mathcal{H}_0 , we transform to a coordinate system rotating in the left-handed sense about the z axis with angular velocity ω ; the phase of the rotation is chosen so that the x axis of the rotating system points along the direction of the left-handed circularly polarized component of \mathcal{H}_1 .

In this rotating system, we take the functions $|M\rangle$ as basis for the representation of the density matrix, and replace ρ in Eq. (7) by $e^{-i\omega S_z t} \rho e^{i\omega S_z t}$; the equation of motion of the MM' element of the density matrix in

the rotating system is now given by

$$\frac{d\rho_{MM'}}{dt} = -i \left[\frac{\mathcal{H}^{\text{rot}}}{\hbar}, \rho \right]_{MM'} + \sum_{NN'} R_{MM'NN'} \times \exp[i\omega(M - M' - N + N')t] [\rho_{NN'} - \rho_{NN'}(T)], \quad (12)$$

where

$$\mathcal{H}^{\text{rot}}/\hbar = (\omega_0 - \omega)S_z + e(S_z^2 - \frac{2}{3}) + hS_x,$$

and where we have ignored the right-handed circularly polarized component of \mathcal{H}_0 . Equation (12), as applied to the nine components of the density matrix, is the starting point for the derivation of the line shape.

The measured quantity in a magnetic resonance experiment is the rate of absorption of microwave power, which is simply given by the time average of $-\omega k \hbar S_y$ in the rotating frame. Thus, we are only interested in the stationary components of the density matrix, since the parts which have a time dependence will average to zero in the expression for the absorption of microwaves. For this reason, we look for solutions of Eq. (12) for which $d\rho/dt = 0$, and ignore all $R_{MM'NN'}$ which contain a time variation, i.e., we require that $M - M' - N + N' = 0$.

B. Relaxation Parameter

Before embarking on the solution of the equations of motion of the density matrix [Eq. (12)], it is instructive to investigate the parameters $R_{MM'NN'}$ and to derive some relations between them. In order to do this, it is necessary to assume a particular form for the interaction $h_i(t)$ between the spins and the lattice; Stevens¹⁴ has discussed the construction of suitable dynamical Hamiltonians for applications in relaxation problems, and it appears to be a reasonable approximation if one chooses a form similar to that for the static strain Hamiltonian. This latter problem is discussed in the Appendix, and it is apparent that the dynamical Hamiltonian should be expressed as a sum over second-rank spin tensors:

$$h_i(t) = \sum_q H_q(t) O_q^{(2)}. \quad (13)$$

The $O_q^{(2)}$ represent the spin operators, and are defined in Eq. (A5), while the $H_q(t)$ are spin-independent. The reason for omitting first-rank spin operators is that the relaxation is expected to take place principally through modulation of the electric field at the ion, such interactions being quadratic in the spin coordinates.

The $J_{MM'NN'}$ of Eq. (9) are now defined as

$$J_{MM'NN'}(\omega) = \sum_{qq'} \langle M | O_q^{(2)} | M' \rangle \times \langle N | O_{q'}^{(2)} | N' \rangle k_{qq'}(\omega), \quad (14)$$

where

$$k_{qq'}(\omega) = \int_0^\infty \langle H_q(t) H_{q'}^*(t-\tau) \rangle e^{i\omega\tau} d\tau. \quad (15)$$

¹⁴ K. W. H. Stevens, Rept. Progr. Phys. **30**, 189 (1967).

The matrix elements of the $O_q^{(2)}$ will be abbreviated by P_q^M , which are defined as follows:

$$\langle M' | O_q^{(2)} | M \rangle = \delta_{M', M+q} \langle M+q | O_q^{(2)} | M \rangle = \delta_{M', M+q} P_q^M. \quad (16)$$

Since the only $J_{MM'NN'}$ of interest are those for which $M-M'=N-N'$, we see that the only $k_{qq'}(\omega)$ which are involved are those for which $q=q'$; we shall assume that $k_{qq}(\omega) = k_{qq}(-\omega)$, and also, by symmetry arguments, we can assume that $k_{qq}(\omega) = k_{-q-q}(\omega)$. Moreover, if the

static Hamiltonian is approximated as $\mathcal{H}_0 = \hbar\omega_0 S_z$, it appears that only three independent $k_{qq'}(\omega)$ are required, namely,

$$k_{00}(0) = K_0, \quad k_{11}(\omega_0) = K_1, \quad k_{22}(2\omega_0) = k_2; \quad (17)$$

therefore, a complete description of the relaxation parameters of the system can be obtained in terms of the three parameters K_0 , K_1 , and K_2 .

Using Eqs. (14)–(17), we see from Eq. (9) that the relevant relaxation parameters $R_{MM'NN'}$ are given by

$$\begin{aligned} R_{MM'M+qM'+q} &= J_{MM+qM'M'+q}(q\omega_0) + J_{MM+qM'M'+q}(-q\omega_0) \\ &\quad - \delta_{q0} \sum_{q''} [J_{q'M+qq''M}((q'-M)\omega_0) + J_{q'M'q''M'+q}((M'-q')\omega_0)] \quad (18) \\ &= 2K_{|q|} P_q^M P_q^{M'} - \delta_{q0} \sum_{q''} [(P_{q'',M})^2 + (P_{q'',M'})^2] K_{|q''|}. \end{aligned}$$

We shall now redefine the individual $R_{MM'M+qM'+q}$ in terms of reciprocal relaxation times, in keeping with the spirit of the Bloch equations. There are three distinct “transverse” relaxation times:

$$R_{1010} = -1/T_2 = -[K_0 + K_1 + \frac{2}{3}K_2], \quad (19)$$

$$R_{1-11-1} = -1/T_3 = -[\frac{2}{3}K_1 + \frac{4}{3}K_2], \quad (20)$$

$$R_{100-1} = -1/T_2' = -\frac{2}{3}K_1, \quad (21)$$

and two distinct “longitudinal” relaxation times:

$$R_{1100} = 1/T_1 = \frac{2}{3}K_1, \quad (22)$$

$$R_{11-1-1} = 1/T_1' = \frac{4}{3}K_2. \quad (23)$$

In order to see which physical processes these relaxation rates describe, it is convenient to consider the time variation due to relaxation of the nine independent operators A_α for an $S=1$ system, using the fact that the average value $\langle A_\alpha \rangle$ is given by $\text{Tr} \rho A_\alpha$. One of the nine A_α 's is the identity operator, whose time derivative is trivially zero; the time derivatives of the remaining eight independent operators can be written as follows:

$$\begin{aligned} \frac{d}{dt} \langle S_z \rangle &= -\left(\frac{1}{T_2} + \frac{2}{T_1'} \right) [\langle S_z \rangle - S_z(0)], \\ \frac{d}{dt} \langle S_\pm \rangle &= -\left(\frac{1}{T_2} + \frac{1}{T_2'} \right) \langle S_\pm \rangle, \\ \frac{d}{dt} \langle S_z^2 - \frac{2}{3} \rangle &= -\frac{3}{T_1} \langle S_z^2 - \frac{2}{3} \rangle, \\ \frac{d}{dt} \langle S_z S_\pm + S_\pm S_z \rangle &= -\left(\frac{1}{T_2} - \frac{1}{T_2'} \right) \langle S_z S_\pm + S_\pm S_z \rangle, \\ \frac{d}{dt} \langle S_\pm^2 \rangle &= -\frac{1}{T_3} \langle S_\pm^2 \rangle. \end{aligned} \quad (24)$$

The first two of these equations (involving S_z , S_+ , and S_-) are the usual Bloch equations; the remaining equations are those involving second-rank spin tensor operators, and are necessary for a description of the relaxation of an $S=1$ system if the symmetry is lower than octahedral. The complete set of Eqs. (24), therefore, represent an extended version of the Bloch equations for an $S=1$ system.

Since each line in Eq. (24) is of the form

$$\frac{d}{dt} \langle A_\alpha \rangle = -\frac{1}{T_\alpha} \langle A_\alpha \rangle,$$

the complete solution for the variation of the system with time can be obtained by solving the equation

$$\frac{d}{dt} \langle A_\alpha \rangle = -\frac{1}{T_\alpha} \langle A_\alpha \rangle + \frac{i}{\hbar} \langle [\mathcal{H}, A_\alpha] \rangle \quad (25)$$

for each A_α . Use of the density matrix in place of the operators A_α gives equivalent equations, but also enables the number of unknown parameters T_α to be reduced from five to three by using Eqs. (19)–(23). In the following, we find the line shape by solving the equations of motion of the density matrix, but we could equally well use Eq. (25).

C. Line Shape

The individual equations of motion of the density matrix can now be written down using Eq. (12) and the definitions of the relaxation times as given in Eqs. (19)–(23). Since the sum of the diagonal elements is a constant, we shall deal with the differences in the diagonal elements Δ_u and Δ_e , rather than the elements themselves, where

$$\Delta_u = \rho_{00} - \rho_{11}, \quad \Delta_e = \rho_{-1-1} - \rho_{00}.$$

In addition, we shall assume that $\hbar\omega_0 \ll kT$, so that the

equilibrium values of these differences can be written

$$\rho_{00}(T) - \rho_{11}(T) = \rho_{-1-1}(T) - \rho_{00}(T) = \Delta_0.$$

Thus, the equations of motion are

$$\begin{aligned} \dot{\Delta}_u = & -\frac{1}{2}\sqrt{2}i\hbar[2(\rho_{10} - \rho_{01}) - (\rho_{0-1} - \rho_{-10})] \\ & - (1/T_1)[2\Delta_u - \Delta_e - \Delta_0] \\ & - (1/T_1')[\Delta_u + \Delta_e - 2\Delta_0]. \end{aligned} \quad (26)$$

$$\begin{aligned} \dot{\Delta}_e = & -\frac{1}{2}\sqrt{2}i\hbar[2(\rho_{0-1} - \rho_{-10}) - (\rho_{10} - \rho_{01})] \\ & - (1/T_1)[2\Delta_e - \Delta_u - \Delta_0] \\ & - (1/T_1')[\Delta_u + \Delta_e - 2\Delta_0], \end{aligned} \quad (27)$$

$$\begin{aligned} \dot{\rho}_{10} = & -i[(\delta + e)\rho_{10} + \frac{1}{2}\sqrt{2}\hbar(\Delta_u - \rho_{1-1})] \\ & - \rho_{10}/T_2 - \rho_{0-1}/T_2', \end{aligned} \quad (28)$$

$$\begin{aligned} \dot{\rho}_{0-1} = & -i[(\delta - e)\rho_{0-1} + \frac{1}{2}\sqrt{2}\hbar(\Delta_e + \rho_{1-1})] \\ & - \rho_{0-1}/T_2 - \rho_{10}/T_2', \end{aligned} \quad (29)$$

$$\dot{\rho}_{1-1} = -i[2\delta\rho_{1-1} + \frac{1}{2}\sqrt{2}\hbar(\rho_{0-1} - \rho_{10})] - \rho_{1-1}/T_3, \quad (30)$$

with three further equations which are the complex conjugates of Eqs. (28)–(30), since one can write $\rho_{ij} = \rho_{ji}^*$ because the density matrix is Hermitian. We have written

$$\delta = \omega_0 - \omega,$$

so that δ represents the displacement from the center of the spectrum, which occurs at the frequency $\omega_0 = \omega$. Sroubek¹⁶ has derived similar equations in his analysis of the DQ transition in this system and the dual frequency experiment of Orton *et al.*² Our equations differ from Sroubek's by the inclusion of the term in T_1' and the cross-relaxation term in T_2' , the latter being essential in order to obtain the IN line.

We solve Eqs. (26)–(30) by equating the time derivatives to zero, and calculating the absorption I of microwaves, which is given by

$$I = -\omega\hbar\langle S_y \rangle = -\omega\hbar \text{Tr} \rho S_y = -\frac{1}{2}\sqrt{2}i\hbar\omega h \times [(\rho_{10} - \rho_{01}) + (\rho_{0-1} - \rho_{-10})]. \quad (31)$$

Obviously, it is straightforward but tedious to calculate I , so we shall simply quote the result as follows (where we write the microwave power as $P = \hbar^2$):

$$I = -2\hbar\omega P \Delta_0 \frac{Ce^2 + E}{e^4 - 2Ae^2 + B}, \quad (32)$$

where

$$\begin{aligned} C &= 1/T_2 - 1/T_2' + PD/T_3, \\ E &= S[\delta^2(1 - 2PD)^2 + C(C + PT_1)], \\ A &= \delta^2(1 - 2PD) - SC - \frac{1}{2}P(T_1S + TC), \\ B &= (E/S)[\delta^2 + S^2 + PST], \end{aligned}$$

and

$$\begin{aligned} D &= [4\delta^2 + 1/T_3^2]^{-1}, \\ S &= 1/T_2 + 1/T_2', \\ T &= [1/T_1 + 2/T_1']^{-1}. \end{aligned}$$

¹⁶Z. Sroubek, Czech. J. Phys. **B11**, 634 (1961).

In connection with this expression, it may be helpful to consider the behavior of I under certain approximations:

(i) In the absence of a zero-field splitting, we put $e = 0$ and find that

$$I(e=0) = -2\hbar\omega P \Delta_0 S / (\delta^2 + S^2 + PST). \quad (33)$$

As is to be expected, $I(e=0)$ gives the usual line shape obtained from the Bloch equations, with effective transverse and longitudinal relaxation times T_2 and T_1 given by

$$1/T_{2B} = S = 1/T_2 + 1/T_2', \quad 1/T_{1B} = 1/T = 1/T_1 + 2/T_1'.$$

(ii) In the limit of vanishingly small power P and no cross-relaxation term, we put $1/T_2' = 0$ and neglect powers of P higher than the first to obtain

$$\begin{aligned} I\left(P \rightarrow 0, \frac{1}{T_2'} = 0\right) &= -\frac{\hbar\omega P \Delta_0}{T_2} \\ &\times \left(\frac{1}{(\delta - e)^2 + 1/T_2^2} + \frac{1}{(\delta + e)^2 + 1/T_2^2} \right). \end{aligned} \quad (34)$$

Again we obtain the expected result, namely, there are two lines at $\delta = \pm e$, with natural linewidths $1/T_2$, corresponding to the transitions $M_s = 1 \rightleftharpoons 0$ and $0 \rightleftharpoons -1$.

(iii) As the microwave power P is increased, the term $PD = P/(4\delta^2 + 1/T_3^2)$ in the expression for I becomes more important; it can be seen that this term arises from Eq. (30), which involves ρ_{1-1} , and therefore represents the DQ transition $M_s = 1 \rightleftharpoons -1$. [It is also worth noting that if there is no strain, Eq. (33) shows that there is no distinct DQ line.]

Equation (32) represents the absorption curve $I(e)$ for a given value of the strain parameter e , and so, in order to obtain the total absorption intensity \mathcal{I} , we must average over a strain distribution function $f(e)$, such that

$$\mathcal{I} = \int_{-\infty}^{\infty} I(e) f(e) de, \quad (35)$$

where

$$\int_{-\infty}^{\infty} f(e) de = 1.$$

$f(e)$ must have a form similar to those given in Eqs. (1)–(3), where $\epsilon = \hbar e$; it was pointed out in our discussion of these equations that all three forms of $f(e)$ are virtually indistinguishable if e is within the turning points of the derivative of f . This is just the case with which we are concerned, for we have only investigated the line shape within the "width" of the NO line; thus, we may choose the most convenient form for $f(e)$, which turns out to be the Lorentzian form

$$f(e) = \frac{W}{\pi} \frac{1}{W^2 + e^2}, \quad (36)$$

since the integration required in Eq. (35) can be performed analytically.

The result of the integration over the strain can be expressed as follows:

$$\begin{aligned} \mathcal{J} &= -2\hbar\omega P\Delta_0 \int_{-\infty}^{\infty} \frac{W}{\pi} \frac{1}{W^2+e^2} \frac{Ce^2+E}{e^4-2Ae^2+B} de, \\ &= -2\hbar\omega P\Delta_0 \\ &\quad \times \frac{CWB^{1/2}+E\{W+[2(B^{1/2}-A)]^{1/2}\}}{\{W^2+W[2(B^{1/2}-A)]^{1/2}+B^{1/2}\}[2B(B^{1/2}-A)]^{1/2}}, \end{aligned} \quad (37)$$

where the parameters A , B , C , and E are defined in Eq. (32).

Unfortunately, this expression for \mathcal{J} does not lend itself easily to approximate simplifications which are reliable over the range of microwave power used in the experiments. However, the following expansion is useful for the case of vanishingly small power P , and when $1/T_2' \ll 1/T_2$; the expansion is valid to terms of first order in P and $1/T_2'$:

$$\begin{aligned} \mathcal{J}(P, 1/T_2' \rightarrow 0) &= -2\hbar\omega P\Delta_0 \left[\frac{W+1/T_2}{\delta^2+(W+1/T_2)^2} \right. \\ &\quad \left. + \frac{1}{WT_2} \left(\frac{W+1/T_2}{\delta^2+(W+1/T_2)^2} - \frac{1/T_2}{\delta^2+(1/T_2)^2} \right) \right]. \end{aligned} \quad (38)$$

The first term represents the NO line, with "effective" relaxation time $1/T_2^* = 1/T_2 + W$; this would be obtained by averaging over e two Lorentzian lines at $\delta = \pm e$ [see Eq. (34)]. The second term is a small correction to this due to the nonzero value of $1/T_2'$. The third term represents a line of width $1/\sqrt{3}T_2$, but the line has a *negative* sign; this, then, represents the IN line. Note that the intensity of the line depends on $1/T_2'$ (the cross-relaxation rate), and the width depends on $1/T_2$ (the width of the individual spin packets of the $M_s = 1 \rightleftharpoons 0$ and $0 \rightleftharpoons -1$ transitions), as is expected from the discussion at the end of Sec. II.

According to Eq. (38), the ratio of the widths of the IN and NO lines is $1/T_2 : W + 1/T_2$; for our sample, the widths are 3 G and 43 G, respectively. The ratio of the heights of the derivative curves is

$$1/WT_2' : 1/(1+WT_2)^2;$$

since $W \gg 1/T_2$, this reduces to $1/T_2' : 1/T_2(1/WT_2)$. It is apparent that, although the IN line represents only a small decrease in absorption, the height of the derivative can easily rival the height of the derivative of the NO line if the inhomogeneous broadening parameter W is large compared to the spin-packet width $1/T_2$; for example, we find that the height of the IN line can be as large as, or even larger than, the height of the NO line.

For larger microwave powers, Eq. (38) is not applicable, but it is apparent that the spin packets will

broaden because of saturation effects; this will have little effect on the NO line, but the IN line broadens and decreases in intensity (see Fig. 4). Also, the DQ line grows at a rate roughly proportional to P^2 , and eventually obliterates the IN line.¹⁶

Before finally making a comparison with experiment for the theoretically predicted line shape represented by \mathcal{J} of Eq. (37), it is necessary to make one correction. So far, we have assumed that the local strains contribute only to the broadening of the $M_s = 1 \rightleftharpoons 0$ and $0 \rightleftharpoons -1$ transitions, with no contribution to the width of the DQ line. This is, to a certain extent, unrealistic, and it is not found possible to obtain a good agreement between theory and experiment for the variation of the DQ line with power. The method of correction that we have adopted is to assume that δ in the expression for \mathcal{J} should be replaced by $\delta + \kappa$, where κ is a small correction due to possible variations in g value or small internal magnetic fields due, for example, to neighboring magnetic impurity ions; κ is assumed to have some distribution function $g(\kappa)$, which we again assume to be Lorentzian, and of the form

$$g(\kappa) = \frac{1}{2T_3^* \pi} \frac{1}{\kappa^2 + (12T_3^*)^2}. \quad (39)$$

We have chosen to call the broadening parameter $1/2T_3^*$ so that the DQ line, which is most affected by this broadening since it is the narrowest line, will have the same type of line shape, viz.,

$$P/(4\delta^2 + 1/T_3^2),$$

but with $1/T_3$ replaced by $1/T_3 + 1/T_3^*$.

Therefore, the over-all line shape is given by

$$A(\delta) = \int_{-\infty}^{\infty} \mathcal{J}(\delta + \kappa) g(\kappa) d\kappa. \quad (40)$$

The correction resulting from the introduction of this type of inhomogeneous broadening represents a very small correction to the NO and IN lines, which justifies the somewhat *ad hoc* method of introducing it; we shall place no particular physical significance on the value obtained for $1/T_3^*$.

The derivative $dA(\delta)/d\delta$ of the line-shape function was evaluated numerically on the University of Minnesota CD 6600 computer, and the various parameters involved were adjusted to fit the experimental results, as discussed in Sec. IV.

IV. EXPERIMENTAL RESULTS

The experiments were performed at a frequency of 9.4 GHz on a standard reflection cavity system with 100

¹⁶ It is necessary to define precisely what is meant by the disappearance of the IN line. We have adopted the simple criterion that there is no inverse line if the derivative of the absorption signal crosses the axis only once, i.e., at the center of the line.

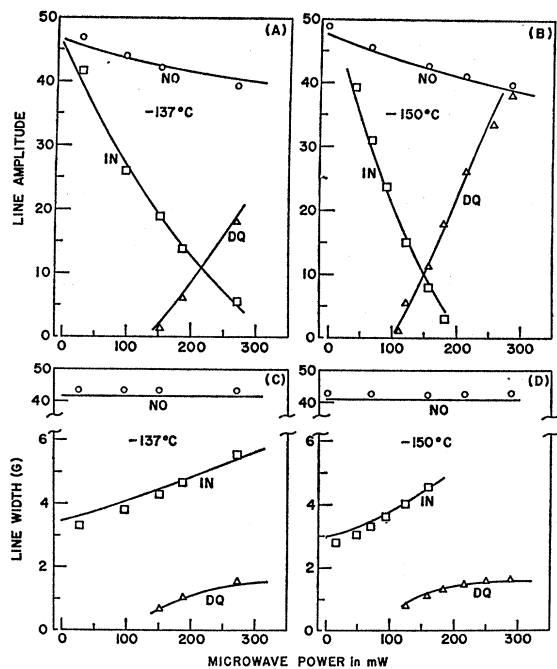


FIG. 3. Comparison of computed and experimental data for derivative amplitudes and linewidths of NO, DQ, and IN lines at -137 and -150°C . Circles, squares, and triangles represent experimental values; solid lines represent computed curves.

kHz phase-sensitive detection. In order that reliable comparisons of signal intensities could be made at various power levels, two calibrated attenuators, R_A and R_B , were used in the microwave system, the former before the cavity, and the latter after the cavity, and just before the crystal detector. R_A determines the power P incident on the sample, while R_B is adjusted so that the same power is always incident upon the detector crystal; in this way, the sensitivity of the detection apparatus should be independent of the power P . The measured height of the line shape is then multiplied by R_A , so that the resulting quantity S is given by

$$S = F \frac{\partial}{\partial \delta} \left(\frac{A(\delta)}{P} \right), \quad (41)$$

where F is a factor depending on the sensitivity of the apparatus, and $A(\delta)$ is the absorption line shape as given in Eq. (40). By this means, if A represented the absorption line shape of a simple unsaturated line, the measured quantity S would be independent of the microwave power P .

Measurements were made at the two temperatures -137 and -150°C , because all three lines (NO, IN, and DQ) are visible within the available range of microwave power; therefore, it is possible to obtain the most accurate values for the relaxation parameters in this temperature range. At 4.2°K the resonance is very readily saturated, and so we have not studied the system at low temperatures in any detail. The width of the NO line

varies with crystal orientation; our results are taken with the magnetic field parallel to one of the fourfold crystal axes, in which direction the linewidth is a maximum.

The measured quantities were the heights and widths of the NO, IN, and DQ lines as a function of microwave power at -137 and -150°C . These quantities were compared with the computed values given by Eq. (41), and the relaxation parameters involved in $A(\delta)$ were adjusted to obtain closest agreement between theory and experiment. The results of the experimental and theoretical comparisons are shown in Fig. 3. In order to make the comparison, the computed line shape had to be scaled to fit the experimentally obtained curves. In addition, a scaling factor for the microwave power P is required, since it is not possible to measure P directly; the scaling factor used agreed closely with the result of a separate experiment on the same cavity.¹⁷

When making the comparisons described above, and illustrated in Fig. 3, it is necessary of course to keep the scaling factors the same for the two different temperatures; in addition, we do not expect that the inhomogeneous broadening parameters should change with temperature. Thus W and $1/T_3^*$ are the same at the two temperatures, while the remaining parameters are allowed to vary. The results of the fit are tabulated in Table I.

However, as a result of the fitting of the parameters, it was found possible to verify the relations between the parameters as derived in Sec. III B; therefore, we made the final fits by assuming that there are only three independent relaxation parameters ($1/T_2$, $1/T_2'$, and $1/T_3$), and that the remaining two are strictly related to them by the relations

$$1/T_1 = 1/T_2' \quad (42)$$

and

$$1/T_1' = 1/T_3 - 1/T_2' \quad (43)$$

[see Eqs. (19)–(23)]. Therefore, in Table I, columns 4 and 5 are related to columns 2 and 3 by Eqs. (42) and (43). The values given in this table are probably accurate to within 10%.

It is therefore possible to obtain values for the parameters K_0 , K_1 , and K_2 , as defined in Sec. III B, and these values are listed in Table II.

In considering these results, it must be pointed out that the over-all line shape varies considerably from sample to sample; therefore, the results given here represent measurements on a particular sample and are not necessarily applicable for all Ni^{2+} in MgO samples. In particular, the linewidth of the NO line varies very markedly, and depends on the history of the sample; for example, the broadest NO line that we have observed was 170 G wide, but after heating the sample at 1300°C for 3 days, followed by cooling to room temperature in

¹⁷ Pamela Wormington and J. R. Bolton (private communication).

TABLE I. Measured values of relaxation rates and strain parameters (in MHz).

Temp.	$\frac{1}{T_2}$	$\frac{1}{T_2'}$	$\frac{1}{T_2}$	$\frac{1}{T_1}$	$\frac{1}{T_1'}$	W	$\frac{1}{T_2^*}$
-137°C	69	10	32	10	22	1013	61
-150°C	53	8	28	8	20		

2 days, the linewidth was reduced to 87 G, which demonstrates that the strains can be substantially modified by heat treatment. Dickey and Drumheller¹⁸ have investigated the effects of local strains in the spectrum of V²⁺ in MgO, and conclude that the strains are probably caused by the presence of V³⁺ ions, which require charge compensation; we have observed apparent changes in the Ni²⁺ concentration after treating the sample, which indicates that Ni²⁺ is probably convertible to other valence states, and so, to a certain extent, the local strains may be caused by the charge compensators of Ni³⁺ (or perhaps Ni⁺) ions. However, further experiments are necessary in order to establish this.

In addition, as the concentration of Ni²⁺ ions increases, dipolar broadening of the line can take place; this type of broadening, unlike strain broadening, will broaden the DQ line ($M_s=1 \rightleftharpoons -1$) as well as the $M_s=1 \rightleftharpoons 0$ and $0 \rightleftharpoons -1$ transitions, and in some cases it is not possible to observe the DQ line because of this effect. The sample from which the results quoted here were obtained was chosen so that all three lines were readily visible, which required the dipolar broadening to be very small, and readily allowed for by the integration over κ in Eq. (40).

V. CONCLUSIONS

We have demonstrated that the use of the density matrix affords a straightforward and successful method of description of the EPR line shape of the Ni²⁺ ion in MgO, and enables relaxation rates to be measured directly from the variation of the over-all line shape with microwave power. In particular, the IN and DQ lines arise naturally from the solution of the equations of motion of the density matrix, and it is apparent that neither of these lines will be visible if there is no inhomogeneous broadening.

The IN line has been identified as being due to an internal cross-relaxation process between the $M_s=1 \rightleftharpoons 0$ and $0 \rightleftharpoons -1$ transitions, and it is perhaps useful at this point to emphasize the distinction between this process

TABLE II. Values of relation parameters K_0 , K_1 , and K_2 (in MHz).

Temp.	K_0	K_1	K_2
-137°C	43	15	17
-150°C	31	12	15

¹⁸ D. H. Dickey and J. E. Drumheller, Phys. Rev. **161**, 279 (1967).

and the more usual type of cross-relaxation process. In general, cross relaxation is said to occur if two spins undergo a mutual spin flip so that energy is conserved, and this can take place via dipole-dipole interactions. For example, if the EPR lines of the two spins overlap to some extent, the result is a change of S_x and S_y (or M_x and M_y) in the rotating coordinate system (rotating about the z axis). In contrast to this situation, the internal cross-relaxation mechanism takes place between two overlapping lines which originate from the *same* spin system. Clearly, this is not a true cross-relaxation effect, but the result must be the same, namely, that the presence of a strain can alter the relaxation rates of S_x and S_y in the rotating frame.

The physical mechanism involved here is not, perhaps, clearly demonstrated by simply solving the equations of motion of the density matrix, and it is best to consider the extended form of the Bloch equations as given in Eqs. (24) and (25). These equations show that, for an $S=1$ system, it is not sufficient to consider only the behavior of the vector quantities S_x , S_y , and S_z , but that the behavior of the tensor quantities $S_x S_y + S_y S_x$, $S_y S_z + S_z S_y$, $S_z S_x + S_x S_z$, $S_x^2 - \frac{2}{3}$, and $S_x^2 - S_y^2$ must also be considered. For example, if the commutator in Eq. (25) is evaluated for $A_\alpha = S_x$ (or S_\pm), it will be found that the rate of change of $\langle S_x \rangle$ contains the term $e(S_x S_z + S_z S_x)$; therefore, the strain parameter e couples the relaxation of the vector operators S_x , S_y , and S_z to the relaxation of the tensor operators ($S_x S_y + S_y S_x$), etc. In this way, it can be seen that, as the strain parameter e is varied, the coupling between the relaxation rates of the two sets of operators is varied, and therefore the apparent rates of relaxation of S_x and S_y in the rotating frame is a function of e . Since the value of e determines the separation of the $M_s=1 \rightleftharpoons 0$ and $0 \rightleftharpoons -1$ transitions for a particular spin, the resulting effect is identical to that of a genuine cross relaxation between the two transitions.

ACKNOWLEDGMENTS

We are greatly indebted to the late Peteris V. Auzins for many useful discussions, and for the initial stimulus which prompted this work. We would also like to thank Dr. T. Cole and Dr. J. J. Lambe for a number of helpful suggestions.

APPENDIX: SPIN HAMILTONIAN FOR Ni²⁺ IN THE PRESENCE OF LOCAL STRAINS

The ground term of Ni²⁺ in our octahedral field is $^3A_2(e^2)$ (using the hole notation), which is an orbital singlet. In order to account for the observed deviation of the g value and to allow for perturbations of the ground state by local strains, we must include the spin-orbit coupling $\mathcal{H}_{C_{60}}$, which will admit the excited states $^3T_2(t_2g)$ and $^1T_2(t_2E)$. The former state will dominate the admixture since it is the lower lying, and we shall neglect the 1T_2 state for simplicity; thus the ground-

state wave function can be written

$$|M\rangle = |^3A_2M a_2\rangle - \sum_{M''j} \frac{\langle ^3T_2M''j | \mathcal{H}_{so} | ^3A_2M a_2 \rangle}{\Delta} \times |^3T_2M''j\rangle, \quad (\text{A1})$$

where M represents the z component of spin $S=1$, and has values 1, 0, and -1 . Δ represents the splitting of the 3T_2 and 3A_2 states; explicit descriptions of these states are given by Griffith.¹⁹ Representing the spin-orbit coupling by $\mathcal{H}_{so} = \sum \xi_0 \mathbf{l}_i \cdot \mathbf{s}_i$, the g value is found to be given by $g = 2.0023 + 4\xi_0/\Delta_0$.

Local deviations from cubic symmetry can be represented by an operator

$$V = \sum_{ikq} C_q^{(2k)} O_q^{(2k)}(\mathbf{l}_i), \quad (\text{A2})$$

where the $O_q^{(2k)}(\mathbf{l}_i)$ are operators of rank $2k$ which operate on the orbital coordinates of \mathbf{l}_i of the i th electrons; only tensors of even rank are included because matrix elements of odd-rank orbital tensors will vanish between $3d$ electronic wave functions (i.e., $C_q^{(2k+1)} \equiv 0$ for all k). We require the matrix elements $\langle M' | V | M \rangle$, where $|M\rangle$ is given by Eq. (A1): Ignoring a constant diagonal energy, we can put $\langle ^3A_2M'a_2 | V | ^3A_2M a_2 \rangle = 0$, and it also turns out that $\langle ^3A_2M'a_2 | V | ^3T_2M''i \rangle = 0$ for all M', M'', i . Therefore,

$$\langle M' | V | M \rangle = \frac{1}{\Delta^2} \sum_{M''i, M'''j} \langle ^3A_2M'a_2 | \mathcal{H}_{so} | ^3T_2M'''j \rangle \times \langle ^3T_2M'''j | V | ^3T_2M''i \rangle \langle ^3T_2M''i | \mathcal{H}_{so} | ^3A_2M a_2 \rangle. \quad (\text{A3})$$

¹⁹ J. S. Griffith, *The Theory of Transition Metal Ions* (Cambridge University Press, London, 1961).

It is possible to make a one-to-one correspondence between the matrix elements $\langle M' | V | M \rangle$ and the matrix elements $\langle M_s' | V_s | M_s \rangle$ of a spin operator V_s , where the states $|M_s\rangle$ are the appropriate states for a spin $S=1$ system. The operator V_s is given by

$$V_s = \sum_q a_q O_q^{(2)}, \quad (\text{A4})$$

where the $O_q^{(2)}$ are second-rank spin tensor operators defined by

$$\begin{aligned} O_0^{(2)} &= S_z^2 - \frac{1}{3}S(S+1), \\ O_{\pm 1}^{(2)} &= \mp (\frac{1}{6}\sqrt{6})(2S_z \mp 1)S_{\pm}, \\ O_{\pm 2}^{(2)} &= (\frac{1}{6}\sqrt{6})S_{\pm}^2, \end{aligned} \quad (\text{A5})$$

and the a_q are related to the $C_q^{(2k)}$ of Eq. (A2) by factors of the order of $(\xi_0/\Delta)^2$; the exact relations are unimportant. The essential point here is that in order to make the correspondence $\langle M' | V | M \rangle = \langle M_s' | V_s | M_s \rangle$, it is not necessary to include any first-rank tensor operators in the expression for V_s in Eq. (A4) (tensors of rank greater than 2 cannot appear, since they will have zero matrix elements for an $S=1$ system); physically, this corresponds to the fact that an electrostatic field cannot have the same effects as a magnetic field (see, for example, Ref. 14).

Thus the full spin Hamiltonian for a site with strain parameters a_q is given by

$$\mathcal{H}_s = g\beta H S_z + \sum_q a_q O_q^{(2)}, \quad (\text{A6})$$

which we have generally approximated by considering only the diagonal part

$$\mathcal{H}_s(\text{diag}) = g\beta H S_z + \epsilon(S_z^2 - \frac{2}{3}),$$

where $\epsilon = a_0$.