Spin-Lattice Relaxation in the $\bar{E}(^2E)$ State of d^3 Ions in Corundum

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A theoretical study of the spin-lattice relaxation in the excited $\bar{E}(^2E)$ state of Cr^{3+} in Al_2O_3 is presented. The two-step resonant relaxation process involving the $2\bar{A}$ state is calculated. The appropriate orbit-lattice parameter appearing in the calculation is obtained from static strain measurements. The theoretical results are in very good agreement with experiment. The normal direct-process relaxation time in the $\bar{E}$ level, involving exchange of phonons whose energy is equal to the Zeeman splitting of $\bar{E}$, is shown to be considerably longer than the radiative lifetime of $\bar{E}$ for an external magnetic field parallel to the c axis. This time can be shortened considerably by a magnetic-field component perpendicular to the c axis. The theory presented is applicable to the corresponding $\bar{E}(^2E)$ states of V^{2+} and Mn^{4+} in Al_2O_3 and with slight modification to the $\bar{E}$ state of these d^3 ions in other crystal hosts.

I. INTRODUCTION

THE spin-lattice relaxation time in the excited $\bar{E}(^2E)$ state of Cr^{3+} and V^{2+} has been the subject of several recent experimental studies.[1-4] In contrast with epr and relaxation studies in ground states, where conventional microwave-resonance techniques apply, the study of the excited states generally involves the use of more sensitive optical double-resonance techniques because of the low populations in these states. However, the theoretical treatment of spin-lattice relaxation in the excited states is in principle no different from that for ground states if the frequency separation between the states being considered is less than the Debye cut-off frequency ν_D. We may expect, then, that the Waller–Kronig–Van Vleck mechanism[5] of spin-lattice relaxation via modulation of the crystalline field by lattice vibrations (the orbit-lattice interaction) will be applicable to the relaxation in excited states such as the ^2E manifold in ruby.

Detailed comparison of Van Vleck's theory with experiment is usually made difficult by the fact that there appear in the orbit-lattice interaction a number of constants whose magnitudes are not at all easy to compute or estimate. The most important of these parameters are those which relate the change in the local crystalline potential to the ligand displacements. In previous theoretical treatments, use has been made of Van Vleck's estimates of these constants, which are based on a simple point-charge model of the crystalline field.

It was generally recognized that these point-charge calculations were inadequate and could at best yield only order-of-magnitude results. More recently, steps have been taken to overcome this difficulty through an independent determination of these constants by static-strain experiments. This is accomplished by measuring the shift of those levels between which relaxation is being considered with externally applied static stress.[6-8] This procedure is valid as long as the phonons involved in the relaxation are of sufficiently long wavelength so that the phonon-produced strain is "macroscopic," and therefore may be related to an externally applied static strain. Note that it is not assumed that the local strain at the paramagnetic center is the same as the bulk strain of the crystal, but that the local strain is the same whether produced by long-wavelength phonons or static strain.

By a fortunate set of circumstances, the calculation of the transition probabilities necessary for the evaluation of the relaxation times in the ^2E state of ruby requires, to first order, only a single constant in the orbit-lattice interaction. In turn, this single constant can be determined from the relative shift of the R_1 and R_2 levels of ruby with externally applied strain, as will be shown in Sec. II.

It will be seen that our calculation, based on this single parameter, gives very good agreement with the experimentally observed two-step "resonant" relaxation

[1] S. Geschwind, G. E. Devlin, R. L. Cohen, and S. R. Chinn, Phys. Rev. **137**, A1087 (1965); S. Geschwind, in *Magnetic and Electric Resonance and Relaxation*, edited by J. Smidt (Interscience Publishers, Inc., New York, 1963).

[2] S. Geschwind, R. J. Collins, and A. L. Schawlow, Phys. Rev. Letters **3**, 544 (1959).

[3] S. Chinn, G. E. Devlin, G. F. Imbusch, and S. Geschwind, Bull. Am. Phys. Soc. **10**, 56 (1965).

[4] W. H. Culver, R. A. Satten, and C. R. Viswanathan, J. Chem. Phys. **38**, 775 (1963).

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

[6] G. D. Watkins and E. Feher, Bull. Am. Phys. Soc. **7**, 29 (1962).

[7] P. L. Donoho and R. B. Hemphill, Bull. Am. Phys. Soc. **7**, 306 (1962); P. L. Donoho, Phys. Rev. **133**, A1080 (1964).

[8] E. R. Feher, Phys. Rev. **136**, A145 (1964); P. G. Klemens, Appl. Phys. Letters **2**, 81 (1963).

process in the $\bar{E}(^2E)$ state both as to magnitude and temperature dependence. It is the agreement with regard to magnitude that is really the significant result, since any interaction which is linear in the thermal strain will produce the proper temperature dependence.

In Sec. III, we will consider the various elements that have been neglected in our calculation, such as odd-parity components of the crystal field, configuration mixing, and noncubic vibrations of the paramagnetic complex. It will be shown that their neglect should not materially affect our result.

In Sec. IV we will consider what is normally called the direct relaxation process between the Zeeman components of $\bar{E}(^2E)$, involving phonons whose energy is equal to the difference in energy between the Zeeman components of $\bar{E}$. At low temperatures, where it becomes competitive with the resonant relaxation process, it will be shown to be sufficiently long so as to be masked by the optical radiative lifetime of the ^2E state.

II. RESONANT RELAXATION PROCESS

A. Basic Relaxation Process

The energy-level diagram of Cr^{3+} in Al_2O_3 is shown in Fig. 1, after Sugano and Tanabe.[9,10] The (cubic field) excited ^2E state is split by the combined action of the trigonal crystalline field and spin-orbit coupling into two Kramers doublets denoted by $2\bar{A}$ and $\bar{E}$, separated by approximately 29 cm^{-1}. In a magnetic field parallel to the c axis, the remaining degeneracy of the doublets is lifted. Experiments[1–3] on the spin-lattice relaxation between the $\bar{E}_+$ and $\bar{E}_-$ levels in the presence of such a magnetic field clearly show a resonant relaxation process. In this process,[11,12] the ion first makes a real transition from $\bar{E}_+$ to $2\bar{A}_-$ (or $2\bar{A}_+$) with the accompanying absorption of a phonon with energy equal to the energy difference of the $\bar{E}_+$ and $2\bar{A}_-$ or $2\bar{A}_+$ states. The process is completed by a transition from $2\bar{A}_-$ (or $2\bar{A}_+$) to $\bar{E}_-$ with the emission of an energy-conserving phonon. Of course the reverse process, in which the ion goes from $\bar{E}_-$ to $\bar{E}_+$ by this two-step process, is also considered. This resonant relaxation process may also be considered as a special case of direct processes in a multilevel system.[13] We therefore have to calculate relaxation rates for the direct process between $2\bar{A}$ and $\bar{E}$, due to the orbit-lattice interaction.

Following the development of Blume and Orbach[14] and Schawlow, Piksis, and Sugano,[15] the orbit-lattice

[9] S. Sugano and Y. Tanabe, J. Phys. Soc. Japan 13, 880 (1958).
[10] Y. Tanabe and S. Sugano, J. Phys. Soc. Japan 9, 753, 766 (1954).
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[14] M. Blume and R. Orbach, Phys. Rev. 127, 1587 (1962).
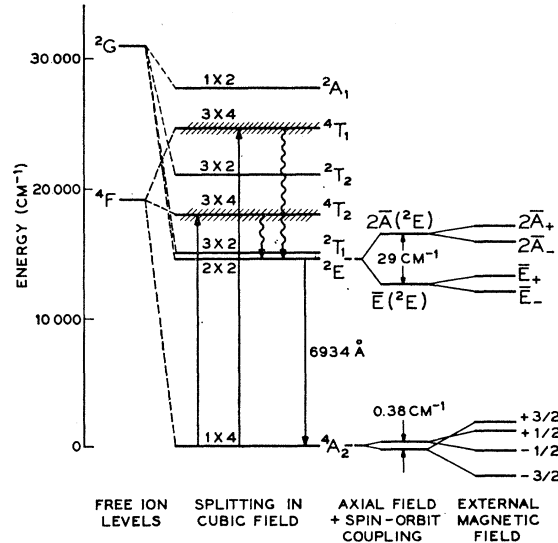[15] A. L. Schawlow, A. H. Piksis, and S. Sugano, Phys. Rev. 122, 1469 (1961).

FIG. 1. Energy-level diagram of Cr^{3+} ion in Al_2O_3 (after Tanabe and Sugano). A similar diagram with appropriate change in scale holds for V^{2+} and Mn^{4+}. The relaxation between $\bar{E}_+$ and $\bar{E}_-$ is considered in this paper.

interaction may be written as

$$\mathcal{H}_{O.L.} = \sum_{\Gamma,m} V(\Gamma)C(\Gamma,m)\epsilon(\Gamma,m). \qquad (1)$$

Here $V(\Gamma)C(\Gamma,m)$ is an orbital operator which transforms as the m component of the Γ representation of the point group at the ion site and $\epsilon(\Gamma,m)$ is a strain which transforms in a similar fashion. $V(\Gamma)C(\Gamma,m)$ may be regarded as the change in energy of the ion due to a change in the local crystalline field which results from a strain $\epsilon(\Gamma,m)$. When ϵ is the dynamic strain produced by the thermal phonons, $\mathcal{H}_{O.L.}$ will produce phonon-induced transitions between the states of the ion. The transition rate from $2\bar{A}$ to $\bar{E}$ with emission of a phonon will then be given by first-order time-dependent perturbation theory as

$$w_{2\bar{A}\to\bar{E}} = 2\pi/\hbar \sum_{\Gamma,m} |\langle\bar{E}|V(\Gamma)C(\Gamma,m)|2\bar{A}\rangle|^2$$
$$\times |\langle n+1|\epsilon(\Gamma,m)|n\rangle|^2 \rho_E, \qquad (2)$$

where ρ_E = density of lattice-oscillator states at energy $E=(E_{2\bar{A}}-E_{\bar{E}})$, and n = occupation number of phonons of energy E.

For phonons of wave vector k, polarization p, velocity $v_{k,p}$, and $E=\hbar\omega$, the expression for ρ_E is

$$\rho_E = V\omega^2 d\Omega/(8\pi^3\hbar v_{k,p}^3). \qquad (3)$$

We make the approximation that the local symmetry about the Cr^{3+} ion is nearly cubic, i.e., that the six oxygen ions nearest to the Cr^{3+} form a regular octahedron. As was shown by Van Vleck,[5] the only even vibrations of such a cluster which need be considered are the E and T_2 vibrations. We will restrict ourselves
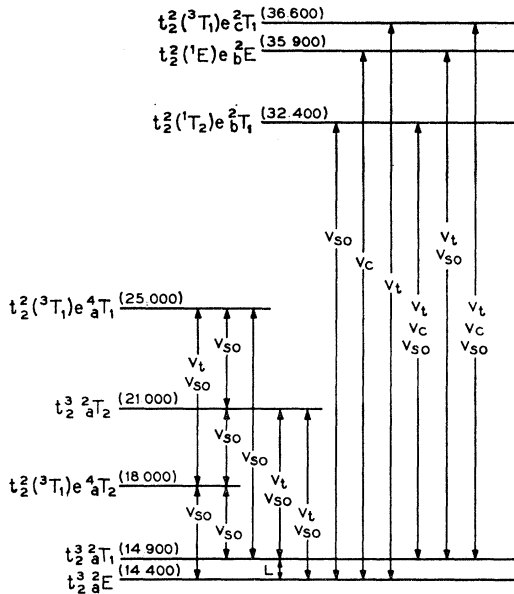
FIG. 2. Excited energy levels of Cr^{3+} in a cubic crystal field. The couplings between the various states are V_{so}=spin-orbit; V_T=trigonal field; V_C=Coulomb interaction. [After Clogston, Phys. Rev. 118, 1229 (1960).]

only to the $t_2{}^3$ configuration in the remainder of this section and postpone treatment of admixture of $t_2{}^2e$ to Sec. III. Matrix elements like $\langle {}^2E|E|{}^2E\rangle$, while allowed by symmetry selection rules, *vanish in a pure* $t_2{}^3$ *configuration*[16] since the reduced matrix element $\langle {}^2E,t_2{}^3||E||{}^2E,t_2{}^3\rangle = 0$. Clearly, by symmetry selection rules, matrix elements $\langle {}^2E|T_2|{}^2E\rangle$ vanish, since $E\times E = A_1+A_2+E$ does not contain T_2. Therefore, we must admix other states into the ^2E manifold of the $t_2{}^3$ configuration to effect coupling with the lattice vibrations. The only remaining doublet states of $t_2{}^3$ are $^2T_1$ and $^2T_2$. By symmetry, the E vibrations cannot connect the $^2T_2$ or $^2T_1$ states with ^2E. Hence, since we wish to consider matrix elements no higher than first order in admixture parameters, only the T_2 vibrations are of interest. While symmetry allows coupling of ^2E to the close lying $^2T_1$ (see Fig. 2) via T_2 vibrations, the *vanishing of the reduced matrix element*[16] $\langle {}^2E,t_2{}^3||T_2||{}^2T_1,t_2{}^3\rangle$ eliminates this interaction. In view of this, *only the $^2T_2$ level need be considered* in calculating the actual wave functions for the ^2E levels in the presence of spin-orbit coupling and axial crystalline field.

B. Wave Functions and Matrix Elements

We now wish to consider the ^2E wave functions as modified by admixtures of the $^2T_2(t_2{}^3)$ by spin-orbit coupling and trigonal field. We then use these to determine the matrix elements of the T_2 vibration within this modified ^2E manifold. We draw heavily from the

[16] Y. Tanabe and H. Kamimura, J. Phys. Soc. Japan **13**, 394 (1958).

work of Tanabe, Sugano, and Kamimura[9,10,16] and use their phase conventions and notations.

The unmodified wave functions of the $\bar{E}$ state are designated $|u_+,-\tfrac{1}{2}\rangle$ and $|u_-,+\tfrac{1}{2}\rangle$ and of the $2\bar{A}$ state, $|u_-,-\tfrac{1}{2}\rangle$ and $|u_+,+\tfrac{1}{2}\rangle$; those of $^2T_2$ are $|x_\pm,\pm\tfrac{1}{2}\rangle$, $|x_\mp,\pm\tfrac{1}{2}\rangle$, and $|x_0,\pm\tfrac{1}{2}\rangle$. The wave functions $|u_+,-\tfrac{1}{2}\rangle$, $|x_+,-\tfrac{1}{2}\rangle$, etc. are the simple product functions

$$|(t_2{}^3)^2Eu_+\rangle|S=\tfrac{1}{2},M_s=-\tfrac{1}{2}\rangle$$

and

$$|(t_2{}^3)^2T_2x_+\rangle|S=\tfrac{1}{2},M_s=-\tfrac{1}{2}\rangle,$$

etc., respectively. The orbital wave functions are defined by

$$
\begin{aligned}
|(t_2{}^3)^2Eu_+\rangle &= -c[(u+iv)/\sqrt{2}] \\
|(t_2{}^3)^2Eu_-\rangle &= -c[(u-iv)/\sqrt{2}],
\end{aligned}
\tag{4a}
$$

where u and v transform like $z^2-\tfrac{1}{2}(x^2+y^2)$ and $\sqrt{3}/2(x^2-y^2)$ respectively, and

$$
\begin{aligned}
|(t_2{}^3)^2T_2x_+\rangle &\rightarrow (c'/\sqrt{3})(\omega yz+\omega^2zx+xy) \\
|(t_2{}^3)^2T_2x_0\rangle &\rightarrow (c'/\sqrt{3})(xy+yz+zx) \\
|(t_2{}^3)^2T_2x_-\rangle &\rightarrow (c'/\sqrt{3})(\omega^2yz+\omega xz+xy),
\end{aligned}
\tag{4b}
$$

where the arrow is to be interpreted as "transforms like" and $\omega=\exp 2\pi i/3$. c and c' are normalization constants. Using the matrix elements of spin-orbit coupling and trigonal field as given in Appendixes AI and AII of Ref. 9, the *modified* ^2E wave functions (which will be denoted by a prime) are given by

$$
|2\bar{A}_+{}'\rangle = |u_+,+\tfrac{1}{2}\rangle + \left(\frac{\zeta}{(\sqrt{6})\Delta}+\frac{(\sqrt{6})K}{\Delta}\right)|x_+,\tfrac{1}{2}\rangle
$$

$$
-\frac{\zeta}{\sqrt{3}\Delta}|x_-,-\tfrac{1}{2}\rangle,
$$

$$
|2\bar{A}_-{}'\rangle = |u_-,-\tfrac{1}{2}\rangle + \frac{\zeta}{\sqrt{3}\Delta}|x_+,+\tfrac{1}{2}\rangle
$$

$$
+\left(\frac{\zeta}{(\sqrt{6})\Delta}+\frac{(\sqrt{6})K}{\Delta}\right)|x_-,-\tfrac{1}{2}\rangle,
$$

$$
|\bar{E}_+{}'\rangle = |u_-,+\tfrac{1}{2}\rangle + \frac{\zeta}{\sqrt{3}\Delta}|x_0,-\tfrac{1}{2}\rangle
$$

$$
-\left(\frac{\zeta}{(\sqrt{6})\Delta}-\frac{(\sqrt{6})K}{\Delta}\right)|x_-,\tfrac{1}{2}\rangle,
$$

$$
|\bar{E}_-{}'\rangle = |u_+,-\tfrac{1}{2}\rangle - \left(\frac{\zeta}{(\sqrt{6})\Delta}-\frac{(\sqrt{6})K}{\Delta}\right)|x_+,-\tfrac{1}{2}\rangle
$$

$$
-\frac{\zeta}{\sqrt{3}\Delta}|x_0,+\tfrac{1}{2}\rangle.
$$

$$\tag{5}$$

We will collectively refer to this set of states as $^2E'$. In Eq. (5) ζ is the one-electron spin-orbit parameter

TABLE I. Clebsch-Gordan coefficients for coupling E to T_2 by T_2 vibrations (taken from Ref. 16).

$$\langle Eu_+ | T_2 x_0 T_2 x_+ \rangle = 1/\sqrt{3}$$
$$\langle Eu_+ | T_2 x_- T_2 x_- \rangle = -1/\sqrt{3}$$
$$\langle Eu_+ | T_2 x_+ T_2 x_0 \rangle = 1/\sqrt{3}$$
$$\langle T_2 x_+ | T_2 x_- Eu_- \rangle = -1/\sqrt{2}$$
$$\langle T_2 u_+ | T_2 x_+ Eu_+ \rangle = 1/\sqrt{2}$$

defined by

$$\zeta = -2\langle x_+,\tfrac{1}{2} | v_{so} | x_+,\tfrac{1}{2} \rangle , \qquad (6a)$$

K the trigonal field parameter by

$$K = \langle x_\pm | v_{\mathrm{trig}} | x_\pm \rangle , \qquad (6b)$$

and Δ is the energy separation between ^2E and $^2T_2$. Using Eq. (5) for $2\bar{A}'$ and $\bar{E}'$ and considering only the T_2 vibration in $\mathfrak{K}_{\mathrm{O.L.}}$ [Eq. (1)], we find that in $\langle E' | \mathfrak{K}_{\mathrm{O.L.}} | 2\bar{A}' \rangle$ we must evaluate matrix elements of the type

$$\langle E,m | \mathfrak{K}_{\mathrm{O.L.}} | T_2,m' \rangle = V(T_2)$$
$$\times \sum_\mu \langle E,m | C(T_2,\mu) | T_2,m' \rangle \epsilon_{-\mu}. \quad (6c)$$

$|E,m\rangle$ and $|T_2,m'\rangle$ must have the same spin states since $\mathfrak{K}_{\mathrm{O.L.}}$ does not involve spin.

By the Wigner-Eckart theorem,

$$\langle \Gamma,m | C(T_2,\mu) | \Gamma',m' \rangle = (\Gamma)^{-1/2}$$
$$\times \langle \Gamma || C(T_2) || \Gamma' \rangle \langle \Gamma m | T_2 \mu \Gamma' m' \rangle , \quad (7)$$

where (Γ) is the dimension of the Γ representation.

Since the C's were defined so that their reduced matrix elements are unity, we have

$$\langle E,m | \mathfrak{K}_{\mathrm{O.L.}} | T_2,m' \rangle = (\sqrt{2})^{-1} V(T_2)$$
$$\times \sum_\mu \langle Em | T_2 \mu T_2 m' \rangle \epsilon_{-\mu} , \quad (8)$$

where the Clebsch-Gordan coefficients are to be found in Table VIII of Tanabe and Kamimura.[16] A listing of these coefficients is to be found in Table I. Using these coupling coefficients and the wave functions in Eq. (5), we find

$$\langle E_\pm' | \mathfrak{K}_{\mathrm{O.L.}} | 2\bar{A}_\pm' \rangle = (\sqrt{2}/3)(\zeta/\Delta)V(T_2)\epsilon_- , \quad (9a)$$

$$\langle E_\pm' | \mathfrak{K}_{\mathrm{O.L.}} | 2\bar{A}_\pm' \rangle = -(2K/\Delta)V(T_2)\epsilon_+ . \quad (9b)$$

The relationship between $(\epsilon_+,\epsilon_0,\epsilon_-)$ and the usual elements of the strain tensor which transform like $T_2(\epsilon_{xy},\epsilon_{yz},\epsilon_{zx})$, is given by Eq. (4b) where $(x_+,x_0,x_-) \rightarrow (\epsilon_+,\epsilon_0,\epsilon_-)$, $(xy,yz,zx) \rightarrow (\epsilon_{xy},\epsilon_{yz},\epsilon_{zx})$, and $c'=1$.

In Eqs. (9), the quantities ζ, Δ, and K are reasonably well known from experimental data while the matrix element of $\epsilon_\mp$ may be expressed (as we shall see below) in terms of known quantities, i.e., the longitudinal and transverse sound velocities and the density of the crystal. We are thus left with the determination of the

reduced matrix element $V(T_2)$. This constant is proportional to the magnitude of the change in potential at a Cr^{3+} site in the crystal which is induced by the oscillating ligands. Early calculations of the relaxation times in paramagnetic ions generally used a point-charge model. The change in electric potential due to arbitrary distortion of the surrounding complex was computed using a point-charge model. In carrying this calculation through there was the difficulty of evaluating the radial integrals and including the effects of covalency (now recognized to be of central importance in crystal-field calculations in transition ions). Some improvements of this technique which avoided the necessity of calculating radial integrals (and partly included covalency) were discussed by Orbach[12] and Kiel,[17] but the basic difficulties remained.

C. Calculation of Relaxation Using Strain Data

Recently these difficulties have been overcome by determining these constants from static-strain experiments. We will now indicate how the constant $V(T_2)$ is determined in our case from the static-strain data on the R lines of ruby. The only difference in $\mathfrak{K}_{\mathrm{O.L.}}$ as given in Eq. (1) for a static strain as compared to a dynamic strain is the time variation of ϵ in the latter case. All other quantities, and in particular $V(T_2)$, are the same in both cases.

The first-order change in the spacing of the $2\bar{A}'$ and $\bar{E}'$ states produced by a static strain is given by

$$\Delta E = \langle 2\bar{A}_\pm' | \mathfrak{K}_{\mathrm{O.L.}} | 2\bar{A}_\pm' \rangle - \langle \bar{E}_\pm' | \mathfrak{K}_{\mathrm{O.L.}} | \bar{E}_\pm' \rangle . \quad (10)$$

Here also for the static case, only strains of symmetry type T_2 will be effective in $^2E'$ for identical reasons to those presented above for considering only the T_2 vibrations in the dynamic case. Again using Table I we find

$$\Delta E = \tfrac{2}{3}(\zeta/\Delta)V(T_2)\epsilon_0 . \quad (11)$$

But ϵ_0 has exactly the symmetry of a strain produced by a stress $T_{z'z'}$ applied along the [111] direction of an octahedron. Labeling the [111] direction z' and with x',y' perpendicular to this axis we have

$$\epsilon_0 = (\sqrt{3})^{-1}(\epsilon_{xy} + \epsilon_{yz} + \epsilon_{zx})$$
$$= (\sqrt{3})^{-1}[\epsilon_{z'z} - \tfrac{1}{2}(\epsilon_{x'x'} + \epsilon_{y'y'})] . \quad (12)$$

To the extent of our approximation that the octahedron of oxygen ions surrounding the Cr^{3+} ion in ruby is regular, this will coincide with the strain produced by a stress $T_{z'z'}$ along the c axis. This strain is related to the stress $T_{z'z'}$ through the compliance elements S_{33} and S_{13} by

$$\epsilon_{z'z'} - \tfrac{1}{2}(\epsilon_{x'x'} + \epsilon_{y'y'}) = (S_{33} - S_{13})T_{z'z'} \simeq \sqrt{3}\epsilon_0 , \quad (13)$$

where the approximately-equal sign refers to the cubic approximation. Substituting the above value of ϵ_0 into

[17] A. Kiel, in *Paramagnetic Resonance* (Academic Press Inc., New York, 1963), Vol. II, p. 525.

Eq. (11), we have

$$(\zeta/\Delta)V(T_2) = (3\sqrt{3}/2)\Delta E/T_{z'z'}(S_{33}-S_{13}). \quad (14)$$

Note that not only have we determined the reduced matrix element $V(T_2)$ in terms of the static-strain data on the R lines and the quantities ζ and Δ, which are fairly accurately known, but that as far as the "spin flip" matrix elements, Eq. (9a), are concerned, even ζ and Δ do not appear, i.e.,

$$\langle \bar{E}_{\pm}'|\mathcal{H}_{\text{O.L.}}|2\bar{A}_{\mp}'\rangle = (\sqrt{\tfrac{3}{2}})$$
$$\times (\Delta E/T_{z'z'})[1/(S_{33}-S_{13})]\epsilon_-. \quad (15)$$

The dynamic strain ϵ is given in terms of phonon creation and annihilation operators by[18]

$$\epsilon_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right) = \left(\frac{\hbar}{8M\omega}\right)^{1/2}$$
$$\times \sum_{kp}(a^*_{k,p}+a_{-k,p})(e_{p,i}k_j+e_{p,j}k_i)e^{ik\cdot r}. \quad (16)$$

Here ϵ_{ij} is the ij component of strain associated with phonons of wave vector k and polarization vector e_p; M is the crystal mass and ω is the phonon angular frequency. The squared matrix elements of the strain are then

$$|\langle \bar{n}_{k,p}+1|\epsilon_{ij}|\bar{n}_{k,p}\rangle|^2 = (\hbar/2M\omega)$$
$$\times (\bar{n}+1)[e_{p,i}k_j+e_{p,j}k_i]^2, \quad (17)$$

where $\bar{n}$ is the phonon occupation number $(e^{\hbar\omega/kT}-1)^{-1}$. $[e_{p,i}k_j+e_{p,j}k_i]^2$ must be averaged over all directions of propagation and polarization. This average has been done by Van Vleck for a cubic crystal. In the spirit of our cubic approximation, we use this average. Finally, using results of Eqs. (3), (15), and (17) in Eq. (2) and performing the indicated averaging, we obtain

$$w_{2\bar{A}\to\bar{E}_+} = \frac{27}{4}\left(\frac{\Delta E}{T_{z'z'}}\frac{1}{S_{33}-S_{13}}\right)^2$$
$$\times \frac{\delta^3}{135\pi\rho\hbar^4}\left(\frac{1}{v_l^5}+\frac{3}{2v_t^5}\right)[\bar{n}+1], \quad (18)$$

where ρ= mass density of the crystal; v_l and v_t are the velocities of the longitudinal and transverse sound waves, respectively; δ=splitting between $2\bar{A}$ and $\bar{E}$ ($\sim$29 cm^{-1} for ruby). From the strain data on the R lines of ruby, Schawlow[19] finds $(\Delta E/T_{z'z'})=5.5\times10^{-11}$ cm^{-1}/(dyn/cm^2); from Huntington's tables[20] of elastic constants, $(S_{33}-S_{13})=0.232\times10^{-12}$ cm^2/dyn; $\rho=4$ g/cm^3; $v_l\sim10^6$ cm/sec; $v_t\sim v_l/\sqrt{3}$. Substituting these

values into Eq. (18) we find, on neglecting $\bar{n}$ compared to 1,

$$w_{2\bar{A}\to\bar{E}_+} = 3.2\times10^7 \text{ sec}^{-1}. \quad (19)$$

The probability of a resonance transition between $\bar{E}_-$ and $\bar{E}_+$ is given by

$$w(\bar{E}_-\to\bar{E}_+) = \frac{w(\bar{E}_-\to 2\bar{A}_-)w(2\bar{A}_-\to\bar{E}_+)}{w(2\bar{A}_-\to\bar{E}_-)+w(2\bar{A}_-\to\bar{E}_+)}$$
$$+\frac{w(\bar{E}_-\to 2\bar{A}_+)w(2\bar{A}_+\to\bar{E}_+)}{w(2\bar{A}_+\to\bar{E}_-)+w(2\bar{A}_+\to\bar{E}_+)} \quad (20)$$

and the relaxation time in the $\bar{E}$ state by

$$T_1 = [w(\bar{E}_-\to\bar{E}_+)+w(\bar{E}_+\to\bar{E}_-)]^{-1}. \quad (21)$$

However, from Eqs. (9a) and (9b), we note that

$$w_{2\bar{A}_{\pm}\to\bar{E}_{\pm}}/w_{2\bar{A}_{\pm}\to\bar{E}_{\mp}} = 18(K/\zeta)^2. \quad (22)$$

Using the recently determined values[21] of $K=233$ cm^{-1} and $\zeta=170$ cm^{-1}, we see that the spin-flip transition $w_{2\bar{A}\to\bar{E}_{\pm}}$ is approximately sixty times slower than the nonspin-flip transition $w_{2\bar{A}_{\pm}\to\bar{E}_{\pm}}$. Therefore, neglecting $w(2\bar{A}_{\pm}\to\bar{E}_{\mp})$ compared to $w(2\bar{A}_{\pm}\to\bar{E}_{\pm})$ and using the fact that $w(2\bar{A}_-\to\bar{E}_-)/w(\bar{E}_-\to 2\bar{A}_-)\sim e^{\delta/kT}$ etc., we find

$$T_1 = [4w(2\bar{A}_-\to\bar{E}_+)]^{-1}e^{\delta/kT}. \quad (23)$$

Thus $w(2\bar{A}_-\to\bar{E}_+)$ can be determined experimentally from the coefficient that appears in front of the exponential factor in the relaxation time. The experimental result for Cr^{3+} in Al$_2$O$_3$ was found to be[1] $w_{2\bar{A}_-\to\bar{E}_+}=6\times10^7$ sec^{-1}. This is in very good agreement with the value 3.2×10^7 sec^{-1} calculated above.

From the experimental value $w_{2\bar{A}_{\pm}\to\bar{E}_{\mp}}$ and (22) we estimate that the much faster nonspin-flip rate $w_{2\bar{A}_{\pm}\to\bar{E}_{\pm}}=3\times10^9$ sec^{-1}, or that the lifetime of the $2\bar{A}$ state against phonon emission would be about $\tau=3\times10^{-10}$ sec. This would give a lifetime determined linewidth of $\Delta\nu=1/2\pi\tau=0.017$ cm^{-1}. This is six times larger than that estimated by McCumber and Sturge from the temperature variation and shift of the R line separation in ruby with temperature.[22] Experiments are under way to measure this quantity directly by magnetic resonance in the $2\bar{A}$ state.

D. V^{2+} and Mn^{4+}

The theory presented above is of course equally applicable to the isoelectronic V^{2+} and Mn^{4+} in Al$_2$O$_3$. The separation δ between $2\bar{A}$ and $\bar{E}$ for these ions is 12.3 cm^{-1} and 80 cm^{-1}, respectively.[23] An interesting test of the above theory would be a comparison of the experimentally determined coefficient in front of the

[18] A. Abragam, *Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961), p. 402 ff.
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[20] H. B. Huntington, in *Advances in Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. VII, p. 213.

[21] R. N. Macfarlane, J. Chem. Phys. **39**, 3118 (1963).
[22] D. E. McCumber and M. D. Sturge, J. Appl. Phys. **34**, 1682 (1963).
[23] M. D. Sturge, Phys. Rev. **130**, 639 (1963); S. Geschwind, P. Kisliuk, M. P. Klein, J. P. Remeika, and D. L. Wood, Phys. Rev. **126**, 1684 (1962).

exponential in the resonant relaxation process, i.e., $(4w_{2\bar{A}\to\bar{E}_+})^{-1}$, for these ions. Referring to Eq. (18) we see that $w_{2\bar{A}\to\bar{E}_+}\sim(\Delta E/T_{z'z'})^2\delta^3$. The δ^3 factor is an expression of the frequency dependence of the direct process in the case where $\delta\gg kT$, i.e., when $\delta\gg kT$ the direct process involves only spontaneous emission of phonons. We may therefore anticipate that in corundum (assuming a Debye spectrum as has been done)

$$\frac{w_{2\bar{A}\to\bar{E}_+}(\mathrm{Cr}^{3+})}{w_{2\bar{A}\to\bar{E}_+}(\mathrm{V}^{2+})}=\frac{(\Delta E/T_{z'z'})^2\,\mathrm{Cr}^{3+}}{(\Delta E/T_{z'z'})^2\,\mathrm{V}^{2+}}\left[\frac{\delta(\mathrm{Cr}^{3+})}{\delta(\mathrm{V}^{2+})}\right]^3 \quad (24)$$

with a parallel expression for Mn^{4+}. Preliminary results on V^{2+} indicate that such a relation is reasonably well obeyed.[24]

Any disagreement between the experimental results and Eq. (24) might be taken as a measure of the departure of the phonon spectrum from the assumed Debye spectrum. It will be especially interesting to test Eq. (24) for Mn^{4+} since here $\delta=80$ cm^{-1} and is therefore quite high up towards the Debye, acoustic limit of 300 cm^{-1}. In addition, the density-of-states curve at 80 cm^{-1} will also reflect the influence of the optical modes.

III. JUSTIFICATION OF THE ONE-PARAMETER MODEL

A. Configuration Mixing

In computing the relaxation effects presented in Sec. II we made a number of simplifying assumptions. Among these were the neglect of the Coulomb interaction (i.e., the assumption of pure $t_2{}^3$ states), the ignoring of odd-parity states and the odd-vibration induced relaxation, and the use of the cubic model. In this section we shall consider these details in turn and show that our previous results are essentially correct. When the Coulomb interaction is included, one finds that the $t_2{}^3$ and $t_2{}^2e$ configurations are mixed. In Fig. 2 we have depicted all the relevant states of the $t_2{}^3$ and $t_2{}^2e$ manifolds and the couplings between them, as given by Clogston.[25]

As a result of these modifications due to the Coulomb interaction we must reconsider some of the interactions which vanished in the pure $t_2{}^3$ case. The amount of admixture of the $t_2{}^2e$ states by the Coulomb interaction will be of the order of $B/(10Dq)\sim0.1$, where B is the usual Racah parameter (~700 cm^{-1}) and $10Dq$ is the crystal field strength $\sim10^4$ cm^{-1}.

The ^2E state will now have a form approximately given by

$$^2E''=\alpha[a(t_2{}^3)^2E+b(t_2{}^2e)^2E+c(t_2{}^2e)^2E]$$
$$+\beta[a'(t_2{}^3)^2T_1+b'(t_2{}^2e)^2T_1+c'(t_2{}^2e)^2T_1]$$
$$+\gamma[a''(t_2{}^3)^2T_2+b''(t_2{}^2e)^2T_2+c''(t_2{}^2e)^2T_2], \quad (25)$$

where again the admixtures of the $^2T_1$ and $^2T_2$ states into ^2E result from spin-orbit coupling and trigonal field.

The coefficients a and the coefficient α are of order unity while all the other coefficients (b,c,β,γ) are about 0.1.[26] Note that now the $^2T_1(t_2{}^3)$ states are mixed into ^2E as a result of the configuration mixing. The discussion of Sec. IIA which led to our considering only the T_2 vibrations remains valid even in the present case. This is so because a $t_2{}^2e$ state cannot couple to a $t_2{}^3$ state via a $V(E)$ interaction since the single-electron matrix element

$$\langle e|V(E)|t_2\rangle$$

vanishes by symmetry. The important matrices occurring in the relaxation process are then,

$$\text{I:}\quad \alpha a\gamma a''\langle(t_2{}^3)^2E|V(T_2)|(t_2{}^3)^2T_2\rangle \quad (26a)$$

$$\text{II:}\quad \alpha a\beta b'\langle(t_2{}^3)^2E|V(T_2)|(t_2{}^2e)^2T_1\rangle$$
$$+\alpha b\beta a'\langle(t_2{}^2e)^2E|V(T_2)|(t_2{}^3)^2T_1\rangle$$
$$+\alpha a\gamma c''\langle(t_2{}^3)^2E|V(T_2)|(t_2{}^2e)^2T_2\rangle$$
$$+\alpha c\gamma a''\langle(t_2{}^2e)^2E|V(T_2)|(t_2{}^3)^2T_2\rangle, \quad (26b)$$

where $V(T_2)=V(T_2)C(T_2,m)$, as before.

The term I is that which was used in Sec. II to compute the relaxation rates, here slightly modified because of the renormalization due to the Coulomb interaction. The terms II are individually much smaller than I since two small parameters (e.g., $\beta b,\gamma c''$) occur in II to only one in I. Altogether they may be expected to make a small contribution since the matrix elements containing $(t_2{}^2e)^2T_1$ are imaginary so that the square of these terms is of second order (i.e., no cross terms). Of the remaining two terms in II, $\alpha a\gamma c''\langle(t_2{}^3)^2E|V(T_2)|(t_2{}^2e)^2T_2\rangle$ will clearly dominate since the $^2T_2$ suffers much stronger configuration mixing than the ^2E (Ref. 26). Calculation of the corresponding cross term shows it to be smaller than I by a factor of about $2c''/a''\simeq0.1$, which we neglect in the following.

Sugano and Peter[27] have calculated the effect of configuration mixing on the splitting of the R_1 and R_2 lines of ruby. They find that the consideration of Coulomb mixing reduces the R_1-R_2 splitting by about 30%. This is the outside limit on error introduced in the calculation of Sec. II due to the assumption of pure $t_2{}^3$ configuration.

B. Odd Vibrations and Noncubic Site Symmetry

Since the Cr^{3+} ion sits at a noncentrosymmetric site, there are present odd components of crystal field which mix in odd-parity states of the type $|(t_{2g}{}^2t_{1u})^2E_u\rangle$ into

[24] S. Chinn, G. F. Imbusch, G. E. Devlin, and S. Geschwind (to be published).
[25] A. M. Clogston, Phys. Rev. 118, 1229 (1960).
[26] M. D. Sturge (private communication) has computed the vectors of the ^2E state, including configuration mixing, using the program of S. Sugano and M. Peter, Phys. Rev. 122, 381 (1961). His exact results justify the estimates we make of the constants in Eq. (25).
[27] S. Sugano and M. Peter, Phys. Rev. 122, 381 (1961).

the even-parity $|(t_{2g}{}^3)^2E_g\rangle$ state. One should examine whether odd vibrations of the octahedron can connect ^2E_u to ^2E_g and therefore play a role in the relaxation. However, $E_g \times E_u = A_{1u} + A_{2u} + E_u$, and none of these vibrations are normal modes of the octahedron,[28] i.e., the only odd vibrations are T_{1u} and T_{2u}. There are, therefore, no contributions from the odd vibrations to the relaxation.

We have analyzed the vibrational modes of the oxygen octahedron which surrounds the paramagnetic impurity as if the site symmetry were perfectly cubic. Actually the local octahedron is severely distorted and the site symmetry is C_3. Our single constant $V(T_2)$ will in reality be decomposed into two independent constants $V(E)$ and $V(A_1)$ of the point group C_3. However, the percentage difference between $V(E)$ and $V(A_1)$ will be of the order of the strength of the trigonal field compared to the cubic field, i.e., $V_{trig}/10Dq$. In corundum $V_{trig} \sim 10^3$ cm^{-1} and $10Dq \sim 10^4$ cm^{-1} so that our approximation of cubic symmetry for the analysis of the relaxation would seem to be a very good one.

IV. THE DIRECT PROCESS

An immediate consequence of Kramers theorem is the fact that any interaction, v, which is invariant under time reversal cannot couple Kramers conjugate states. It is also true that even in an arbitrary magnetic field, v will not couple the states of an *isolated* Kramers doublet (by Kramers doublet we mean time-reversed states for a system with an *odd* number of electrons). This may be seen as follows: In a magnetic field, the Kramers conjugate states $|+\rangle$ and $|-\rangle$ are mixed so that the proper states of the doublet can be written as

$$\psi_+ = a|+\rangle + b|-\rangle, \qquad (27a)$$

$$\psi_- = -b|+\rangle + a|-\rangle, \qquad (27b)$$

and the matrix element of v becomes

$$\langle\psi_+|v|\psi_-\rangle = ab(\langle+|v|+\rangle - \langle-|v|-\rangle) \qquad (28)$$
$$\equiv 0.$$

The last statement follows from application of the time conjugation operator. Therefore, an electric potential can couple the states of a Kramers doublet directly only when the magnetic field mixes other Kramers doublets into the states under consideration. This situation is of course quite different from the resonant process considered earlier where the phonons couple the two different doublets.

In a parallel magnetic field, there is no mixing of the $2\bar{A}'$ and $\bar{E}'$ states, i.e., $\langle 2\bar{A}'|L_z + 2S_z|\bar{E}'\rangle = 0$. This is so, since, as seen earlier, there are no matrix elements of L in the pure E state and in addition $\langle(t_2{}^3)^2E|L|(t_2{}^3)^2T_2\rangle = 0$ (see table on p. 399 in Ref. 16). However, if we consider

configuration mixing, then there will be an admixing of $2\bar{A}''$ into $\bar{E}''$ by an external field parallel to the c axis via the matrix element $\langle(t_2{}^3)^2E|L_z|(t_2{}^3)^2T_1\rangle$. In accord with the notation of Eq. (25), the coefficient of admixture will be of order $[\beta'(\mu H/\delta)]$ where μH is the Zeeman energy (~ 1 cm^{-1}), δ is the separation of $2\bar{A}$ and $\bar{E}$ (~ 29 cm^{-1} for Cr^{3+}). The calculation of Sturge[26] shows $\beta' \sim 0.15$. This will give rise to a direct relaxation rate between $\bar{E}_+''$ and $\bar{E}_-''$ which, in analogy to Eq. (2), can be written

$$W_{\bar{E}_+'' \to \bar{E}_-''}(\text{direct}) = 2\pi/\hbar |\langle 2\bar{A}|\mathcal{3C}_{\text{O.L.}}|\bar{E}\rangle|^2$$
$$\times |\langle\bar{n}+1|\epsilon|n\rangle|(\alpha\beta'\mu H/\delta)^2 \times^2 \rho_E, \quad (29)$$

where now the density-of-states factor ρ_E and $\bar{n}$ are to be evaluated at an energy equal to μH instead of δ as before. A numerical evaluation shows that T_1 is in the range of

$$T_1 \sim (1.0/T) \text{ sec (deg K)}^{-1}. \qquad (30)$$

This is far too long to observe in the presence of the much faster radiative lifetime of ^2E in ruby of 3.5 msec.

There are a number of additional terms which may be mixed by L_z but these are all smaller than L_z by factors like $(\delta/\Delta)^2$. Such terms were considered by Kiel in an earlier publication,[29] but he missed the time-reversal cancellation by an improper application of the time conjugation operator. In essence, Eq. (6) in Kiel's paper should be multiplied by $(\mu H/\delta)^2$ so that the T_1 of 3.5 msec that he calculates will now be of the order of seconds.

However, the situation for the direct process is quite different if the magnetic field has a component perpendicular to the c axis of the crystal. In this case there are matrix elements of the operator $H_\perp S_x$ between the ^2E part of the $\bar{E}$ state and the ^2E part of the $2\bar{A}$ state. This admixture will be of order $\beta H_\perp/\delta$, and the direct process may then be sufficiently rapid to be observable. To calculate this rate we first give the first-order effect of the perpendicular field on the wave functions (1). Denoting the perturbed states by $\Psi(\bar{E}+)$ and $\Psi(\bar{E}-)$, and setting $H_{||} = H \cos\theta$, $H_\perp = H \sin\theta$, where θ is the angle between the field and the c axis, we find

$$\Psi(\bar{E}_+') = |\bar{E}_+'\rangle - (\beta H \sin\theta/\delta)|2\bar{A}_-'\rangle,$$
$$\Psi(\bar{E}_-') = |\bar{E}_+'\rangle - (\beta H \sin\theta/\delta)|2\bar{A}_+'\rangle, \qquad (31)$$

where $|\bar{E}_-'\rangle$, $|2\bar{A}_+'\rangle$, etc., are given in (5). The electronic part of the matrix element of the orbit-lattice interaction between these two states is then

$$\langle\Psi(\bar{E}_-)|\mathcal{3C}_{\text{O.L.}}|\Psi(\bar{E}_+)\rangle$$
$$= -(\beta H \sin\theta/\delta)(4K/\delta)V(T_{2g})\epsilon_{+1}, \quad (32)$$

where configuration interaction is neglected. Calculation of the phonon matrix elements will finally give for the

[28] L. D. Landau and E. M. Lifshitz, in *Quantum Mechanics, Non-Relativistic Theory* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1958), p. 366.

[29] A. Kiel, in *Advances in Quantum Electronics*, edited by J. R. Singer (Columbia University Press, New York, 1961), p. 417.

direct-process relaxation time

$$\frac{1}{T_1}=\frac{8K^2}{15\Delta^2}|V(T_{2g})|^2\frac{g_{||}{}^3\beta^5H^5\cos^3\theta\sin^2\theta}{15\rho\hbar^4\delta^2}\left(\frac{1}{v_l{}^5}+\frac{3}{2v_t{}^5}\right)$$
$$\times\coth\left(\frac{g_{||}\beta H\cos\theta}{2kT}\right). \quad (33)$$

The field at 45° to the c axis large enough for a resonance at 35 kMc/sec is of the order of 13 kG. The hyperbolic cotangent is essentially unity for this frequency at 1°K. Substituting the appropriate constants, we find, at this temperature and frequency, $T_1=40$ msec. It is clear that increasing the frequency of measurement from 35 to 70 kMc/sec would reduce this time to 1.25 msec at 1°K, since $T_1\propto H^{-5}$. Further, any contributions to the matrix elements from configuration mixing would most likely tend to increase the relaxation rate. It seems just barely possible, then, that the direct relaxation process can be made to give a relaxation time shorter than the 4 msec optical lifetime of the $\bar{E}$ states of ruby. Experiments are underway to determine this.

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Line Shapes of Resonant, Nonlinear, Paramagnetic Susceptibilities

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Line shapes for both the absolute value and the real and imaginary components of the nonlinear, paramagnetic susceptibility $\mathfrak{X}_{NL}(2\omega)$ of a ruby crystal have been measured as a function of the magnetic field and crystal orientation at room temperature and "resonant" conditions, where the X-band driving frequency coincides with or is very close to the resonance frequencies of an equidistant or nearly equidistant paramagnetic three-level system. Though all measured line shapes were in good qualitative agreement with theoretical line-shape expressions, derived under the assumption of homogeneously broadened, Lorentzian-shaped, single-quantum resonances, a quantitative comparison between theory and experiment exhibited systematic discrepancies, such as too slowly decaying wings for the theoretical curves and too large theoretical amplitudes at "partly resonant" conditions for nearly equidistant three-level schemes. Line-shape measurements for single-quantum resonances of the linear susceptibility contradicted the Lorentzian line-shape assumption, but could satisfactorily be matched by a Gauss-type line shape. Although it was possible to fit the measured single-quantum resonance line shapes also by the convolution of a narrow, Lorentzian line shape with a proper combination of macroscopic inhomogeneous line-broadening effects such as Gaussian distributions of crystal c-axis orientations and crystal strains, the equivalent procedure for the nonlinear susceptibility resonances did not remove the discrepancy between theory and experiment. Since the approach towards thermal equilibrium within tightly coupled spin systems in solids has, in general, to be described by nonexponential relaxation processes, the line-shape expressions for the nonlinear susceptibility $\mathfrak{X}_{NL}(2\omega)$ were phenomenologically generalized and formulated in terms of non-Lorentzian-shaped, homogeneous, single-quantum resonances. By using these generalized line-shape expressions, it was possible to achieve a satisfactory quantitative agreement with all experimental results for both the line shapes of single-quantum, linear-susceptibility resonances as well as for the line shapes of the absolute value and the real and imaginary components of the nonlinear-susceptibility resonances.

I. INTRODUCTION

THE excessive driving-power requirements, necessary for the observation of frequency-mixing or harmonic-generation effects due to nonlinear magnetic or electric (quantum) susceptibilities at nonresonant conditions, can be considerably reduced if one or several of the mixing frequencies are close to the resonance frequencies of the mixing medium. In particular, the nonlinear-susceptibility-frequency mixing effect can be observed at relatively low-power levels, if all mixing frequencies coincide or are very close to the quantum-mechanical resonances of a three-energy-level system. For this case the excitation frequencies will predominantly generate a nonlinear polarization component, oscillating with the sum or difference frequency, which coincides with the third transition frequency, provided all possible transitions within the three-level system are quantum-mechanically allowed. The special case of harmonic generation by means of the "resonant" nonlinear susceptibility of an equidistant paramagnetic three-level scheme in a ruby crystal at room tempera-