Solid-state masers without inversion: Theoretical prediction for high-efficiency oscillators or phase-sensitive detectors

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Analytic steady-state solutions of the density-matrix equation are derived by means of a formalism suitable for multilevel spin systems in dilute paramagnetic solids at high temperature and subjected to several strong fields. It is shown that solid-state masers without inversion may be obtained in the presence of one, two, or three quasimonochromatic strong fields at resonance. In the usual cases of two fields, the maser action with or without inversion cannot achieve high-efficiency microwave generation or detection, since for strong emitted fields, the saturating and nonlinear effects are strong too. On the contrary, whenever three frequency-correlated fields fulfill the "spectroscopic bridge" conditions, the saturating effects do not occur, and linear effects prevail, even when all these fields are strong. In this case, high-efficiency microwave generations or phase-sensitive detections may be achieved.

I. INTRODUCTION

There has recently been considerable interest in the study of lasers without population inversion, and many schemes for such systems have been proposed.[1] In the case of maser effects, as it has been demonstrated some time ago, the results cannot be predicted from a treatment based on the population difference alone.[2] In the cases of laser and maser effects mentioned above, the applied fields are considered monochromatically and their frequencies are not exactly at resonance.

The purpose of this present paper is to show that in the case of dilute paramagnetic solids, masers without population inversion may be realized in the presence of one, two, or three quasimonochromatic strong fields at resonance. In addition, some spin systems in suitable host lattices, considering that all the "spectroscopic bridge" conditions are satisfied, could be special cases of solid-state masers without inversion, which do not exhibit the limitations as saturating or nonlinear effects, which up to now have resulted in a virtual cessation of development in the solid-state maser field.[3]

II. FORMALISM

In order to obtain the microwave powers absorbed or emitted by a dilute paramagnetic solid subjected to several quasimonochromatic fields at resonance, one can use the analytic steady-state solutions of the density-matrix equation for a multilevel spin system:[4]

$$P_{nm}=\int P_{nm}(\omega_{nm})D_{nm}(\omega)d\omega=2\hbar\omega^0_{nm}N\Omega_{nm} \ . \tag{1}$$

If $P_{nm}>0$, the power is emitted, while if $P_{nm}<0$, the power is absorbed. $\omega^0_{nm}=\omega^0_n-\omega^0_m$, $\omega^0_n=(E_n/\hbar)$, with E_n being the exact eigenvalues of the spin Hamiltonian and N the total number of spins. $\omega_{nm}=\omega^0_{nm}+\delta\omega$, where the spectral density $D_{nm}(\omega)$ of the quasimonochromatic field at resonance is nonvanishing as long as $|\delta\omega|\ll(T_2^{mn})^{-1}$, where T_2^{mn} is the spin-spin relaxation time corresponding to the pair of levels involved. The power parameters $\Omega_{nm}=-\Omega_{mn}$ are obtained by solving the equations

$$\rho_{mm}-\rho_{nn}=\Omega_{mn}\langle p^2_{mn}\rangle^{-1}\left\{(T_2^{mn})^{-1}+\sum_{\sigma\neq m,n}[T_2^{\sigma m}\langle p^2_{n\sigma}\rangle+T_2^{n\sigma}\langle p^2_{\sigma m}\rangle]\right\}-\sum_{\sigma\neq m,n}[\Omega_{n\sigma}T_2^{\sigma m}+\Omega_{\sigma m}T_2^{n\sigma}] \ , \tag{2}$$

$$\chi_\sigma=\rho_{\sigma\sigma}-\rho^0_{\sigma\sigma}=2\sum_{i,j}K^\sigma_{ij}\Omega_{ij}; \quad i<j \ , \tag{3}$$

where the diagonal elements of the density matrix $\rho_{ii}=(N_i/N)$, N_i being the population of the spin level i, while ρ^0_{ii} are the thermal equilibrium values of ρ_{ii}. p_{ij} are matrix elements (considered to be real) of the time-dependent Hamiltonian which represents the interactions of the multilevel spin system with the microwave fields. They are expressed in $\hbar$ unit and are written in the interaction representation like the off-diagonal elements ρ_{ij} of the density matrix. $\langle p^2_{ij}\rangle=\int p^2_{ij}(\omega_{ij})D_{ij}(\omega)d\omega$, and the "power parameters"

$$\Omega_{ij}=\int p_{ij}(\omega_{ij})Q_{ij}(\omega_{ij})D_{ij}(\omega)d\omega \ ,$$

where Q_{ij} is the imaginary part of ρ_{ij}. We have to emphasize that Ω_{ij}, unlike p_{ij} and Q_{ij}, are observable quantities and include only $\langle p^2_{rs}\rangle$ [see Eq. (2)]. The spin-lattice relaxation times K^σ_{ij} are obtained by solving the equations

$$\sum_{i\neq m}(K^i_{mn}w_{im}-K^m_{mn}w_{mi})=\sum_{i\neq n}(K^n_{mn}w_{ni}-K^i_{mn}w_{in})=1 \ ;$$

$$\sum_{i\neq j}(K^j_{mn}w_{ji}-K^i_{mn}w_{ij})=0, \quad j\neq m,n \ , \tag{4}$$

where w_{ij} are spin-lattice relaxation rates corresponding to the pair of states i,j. K^i_{mn} have the following properties:

$$\sum_i K^i_{mn}=0;\quad K^i_{mn}=-K^i_{nm};\quad K^i_{mn}=K^i_{m\sigma}+K^i_{\sigma n}\ . \tag{5}$$

Let us now note the conditions that have to be fulfilled so that Eqs. (2)–(4) are valid. Thus in a recent paper,[4] it is proved that only for fewer than four quasimonochromatic fields at resonance, the results for the power parameters Ω_{nm} given by the equations mentioned above are the same as those obtained when the microwave fields are considered monochromatically, replacing p^2_{ij} by $\langle p^2_{ij}\rangle$. At low temperatures, the direct spin-lattice relaxation processes dominate, so that the spin-spin relaxation rates are much faster than the spin-lattice relaxation rates. In this case, the microwave fields may not be very strong, so in Eqs. (2)–(4) for the relaxation rates mentioned above one can take into account the results of the usual theories of relaxation.[5–7]

At higher temperatures, the spin-spin and spin-lattice relaxation rates become comparable and the EPR linewidths have strong temperature dependences.[8] In this case, when some conditions are satisfied (see Sec. IV), strong microwave fields are needed. As we have shown,[9] at higher temperatures, or for very strong microwave fields, the usual theories of relaxation that are based on the concept of correlation function,[5,6] and that are often referred to as Redfield theory,[7] are not appropriate for multilevel spin systems in dilute paramagnetic solids. So we have extended here the method applied to S electron ions,[10] which considers the relaxation mechanisms at higher temperatures as direct spin-lattice relaxation processes, but not for the spin system, since we have included in the static Hamiltonian, the vibrational energy of the paramagnetic impurity. Considering the interaction representation in a direct density matrix treatment, unlike the usual relaxation theories, the interaction with the phonon fields of the lattice and with the microwave fields is treated simultaneously. This treatment enables us to consider the cases of strong or even very strong microwave fields. In the hypothesis that the lattice has an infinite specific heat, the spin system is decoupled from the vibrational excitations, and although the oscillators relax via absorption or emission of one phonon, the results are similar to those obtained when the spin system is considered to relax via absorption and emission of two phonons simultaneously (Raman or two-phonon relaxation processes[11]). The results for the spin-spin relaxation rates $-R_{mn}=(T^{mn}_2)^{-1}$ are similar to those given by the Redfield theory, the difference being that the contributions of the spin-lattice relaxation processes to the pseudodiagonal elements of the relaxation rates R_{mn} have to be multiplied by a narrowing factor of about one-half. The concept of relaxation matrix and consequently Eqs. (2)–(4) remains valid as long as[9]

$$\langle p^2_{mn}\rangle/(R_{ik}R_{mn})\ll 1\ . \tag{6}$$

$-R_{ik}$ are relaxation rates corresponding to the pair of different vibrational states and represent the linewidth in the infrared (IR) spectra. As $-R_{mn}$, which corresponds to the EPR linewidth, is of few G (10^{-4} cm^{-1}), the condition (6) is satisfied even for very strong microwave fields whose magnetic amplitudes do not, however, exceed a few hundred G. When the condition (6) is not satisfied, only the spin-lattice relaxation rates w_{ij} are changed, they depend now on the field intensities,[9] but in his case Eqs. (2)–(4) cease to be valid.

III. DOUBLE RESONANCE: NONLINEAR EFFECTS IN TWO STRONG FIELDS

In the case of a single microwave field, and two or three fields at resonance, corresponding to transitions that have no levels in common [the electron-electron double resonance (ELDOR) case: $m,n\neq i,j$], the solutions of Eq. (2) are

$$\Omega_{mn}=\langle p^2_{mn}\rangle T^{mn}_2(\rho_{mm}-\rho_{nn})\ . \tag{7}$$

If $E_m>E_n$ and $\rho_{mm}<\rho_{nn}$, the microwave power is absorbed [see Eq. (1)], while if $\rho_{mm}>\rho_{nn}$, the power is emitted. That is why in the ELDOR case the maser effects may occur only when the population inversion is realized.

When two microwave fields correspond to transitions that have a level in common [the electron-nuclear double resonance (ENDOR) case], we can take into account two limiting cases.

At low temperatures, the spin-spin relaxation times T^{mn}_2 are usually much shorter than the spin lattice relaxation times: $T^{mn}_1=K^n_{mn}-K^m_{mn}$. In this case the saturating power of the pumping field of frequency ω_{ij} is obtained for[4] $T^{ij}_1T^{ij}_2\langle p^2_{ij}\rangle\gg 1$. As $T_2\ll T_1$, the solutions (7) for the power parameters remain the same, and ENDOR and ELDOR cases become similar. These are the usual cases of masers with inversion.[3] As at relative low temperature, T^{mn}_2 are usually temperature independent, and $(\rho^0_{mm}-\rho^0_{nn})$ increases when the temperature decreases, the lower temperature, the higher emitting powers, and signal-to-noise ratio occur. Unfortunately, as at low temperatures T^{mn}_1 are very long, because of the saturating effects, the pumping power and consequently the emitted power is low. In order to obtain higher emitted power, higher temperatures are needed. At higher temperatures, the spin-spin and spin-lattice relaxation times become comparable and the EPR linewidths have in some cases, strong temperature dependences.[8] That is why in the ENDOR case at higher temperatures, the summations in Eq. (2) are not negligible, and consequently the solutions (7) for the power parameters cease to be valid. As we have shown, when some conditions are fulfilled,[4] emitted powers can be obtained even when the population inversion is not achieved. However, although at high temperatures the ELDOR case is better than the ENDOR case,[4] the efficiency of amplification is low, the emitting power is not high, while the heat absorbed by the lattice is high. The better amplification is achieved when the linear effects prevail,[3] so that the emitting power has to be proportional to the intensity of the emitted field. In this case this intensity has to be, in all of the cases mentioned in this section, much lower than the intensity of the saturating field. When both fields are strong, the nonlinear effects prevail. When the saturation is reached, the power absorbed or emitted by the crystal is maximum, and both become independent on the intensities of the two strong fields.

The heat absorbed by the lattice per unit time is

$$P_L = -(P_a + P_e) = \sum_{j>i} (E_j - E_i)(w_{ji}\chi_j - w_{ij}\chi_i) , \quad (8)$$

where P_a and P_e are the powers absorbed and emitted by the crystal, χ_i being given by Eq. (3). Since in the double-resonance case the efficiency of the crystal $\eta = -(P_e/P_a)$ is usually very low, P_a, $|\chi_i|$, and P_L are all proportional to the absorbing power parameter and consequently, they reach their maximum values when the pumping transition is saturated. That is why a fundamental question arises from the remarks mentioned above: *Is it possible that the nonlinear or saturating effects do not occur when all of the pumping and emitted fields are very strong and the heat absorbed by the lattice per unit time is minimum?*

IV. TRIPLE RESONANCE: LINEAR EFFECTS IN THREE STRONG FIELDS

A. Three frequency-correlated fields

Let us consider three strong quasimonochromatic fields at resonance, whose frequencies are correlated: $\omega_{nm} = \omega_{n\sigma} + \omega_{\sigma m}$, so that

$$({}^{rs}_{ij}\delta_1)^{-1} = T_2^{ij} T_2^{rs} \langle p_{ij}^2 \rangle \gg 1 ; \quad (9a)$$

$$|{}^{rs}_{ij}\delta_2| = |(\langle p_{ij}^2 \rangle - \langle p_{rs}^2 \rangle)\langle p_{ij}^2 \rangle^{-1}| \ll 1 , \quad (9b)$$

where ij and rs are $mn, n\sigma, \sigma m$ by circular permutations.

Considering the properties (5) in Eq. (3) one obtains

$$\chi_i = 2K^i_{n\sigma}\Omega^{n\sigma}_{mn} + 2K^i_{\sigma m}\Omega^{\sigma m}_{mn} , \quad (10)$$

where $\Omega^{n\sigma}_{mn} = \Omega_{n\sigma} - \Omega_{mn}$.

Let $X_{mn} = {}^{mn}_{mn}\delta_1 T_2^{mn} + {}^{n\sigma}_{mn}\delta_2 T_2^{\sigma m} + {}^{\sigma m}_{mn}\delta_2 T_2^{n\sigma}$ ($X_{n\sigma}$ and $X_{\sigma m}$ being obtained by circular permutations) and the solutions for the power parameters of the form $\Omega_{ij} = (\Delta_{ij}/\Delta)$. It is easy to find that,[4] in the case of three frequency-correlated fields Δ_{ij} and Δ contain terms that are proportional only to X_{ij}, $X_{ij}X_{rs}$, or X_{ij}, $X_{ij}X_{rs}$, and $X_{ij}X_{rs}X_{uv}$, respectively, where ij, rs, and uv are mn, $n\sigma$, and σm by circular permutations. Let us assume that these fields are strong so that the conditions (9) hold. Consequently, we may retain in Δ_{ij} and Δ only the terms proportional to X_{ij}. In this case $\Delta_{n\sigma} - \Delta_{mn}$, $\Delta_{\sigma m} - \Delta_{mn}$, and Δ are proportional to $X = X_{mn} + X_{n\sigma} + X_{\sigma m}$. Ω^{rs}_{ij} in Eq. (10), the populations, and the heat absorbed by the lattice become independent on X and consequently, on the intensities of the three strong fields, and all of them reach their minimum values. On the contrary, Ω_{ij} and the microwave powers emitted or absorbed by the crystal are proportional to X_{ij}, but not to X, so they could depend strongly on the intensities of these fields. That is why, the cases mentioned at the end of the previous section become possible.

B. The spectroscopic bridge

Thus, an interesting case is that of the spectroscopic bridge:[12] $E_n > E_\sigma > E_m$ and $\langle p_{\sigma m}^2 \rangle = \langle p_{n\sigma}^2 \rangle$. Let us denote

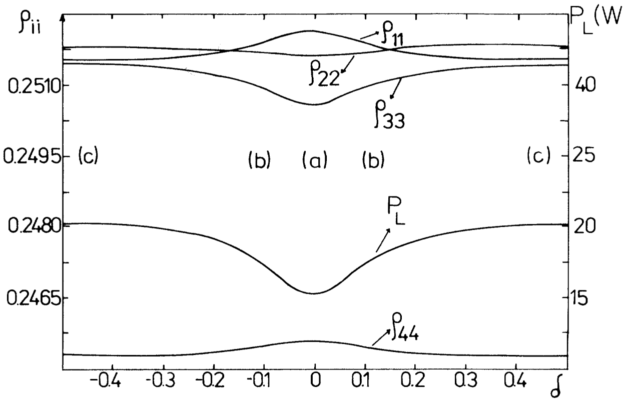

FIG. 1. The predicted dependences (Ref. 14) on δ of the level populations ρ_{ii} and of the heat absorbed by the lattice per unit time P_L.

$$\delta = [\langle p_{mn}^2 \rangle - \langle p_{n\sigma}^2 \rangle + (T_2^{\sigma m})^{-1}(T_2^{n\sigma})^{-1}]\langle p_{n\sigma}^2 \rangle^{-1} . \quad (11)$$

We can easily find that the population parameters $\Omega^{n\sigma}_{mn}$ and $\Omega^{\sigma m}_{mn}$ contain terms that are proportional to δ_1 and δ^n ($n \geq 2$), but as a consequence of the properties (5) they do not contain any term proportional to δ. Consequently, the populations and the heat absorbed by the lattice do not depend for small δ on the sign of δ (see Fig. 1). On the contrary, the power parameters Ω_{ij} and consequently P_{ij} include terms proportional to δ. When $\delta < 0$, $P_{n\sigma}$, $P_{\sigma m}$ are absorbed and P_{mn} emitted, while for $\delta > 0$, $P_{n\sigma}, P_{\sigma m}$ are emitted and P_{mn} is absorbed (see Fig. 2). Thus, although P_{mn} is proportional to $(\rho_{mm} - \rho_{nn})$ and $\rho_{nn} < \rho_{mm}$ (see Fig. 1), when $\delta < 0$, P_{mn} is emitted (see Fig. 2), since it is also proportional to δ. That is why, the spectroscopic bridge acts as a maser without inversion. In Figs. 1(a) and 2(a), ${}^{ij}_{rs}\delta_1$ and ${}^{rs}_{ij}\delta_2$ are very small and in this case, P_{ij} are proportional to δ. If $\delta = 0$, $P_{mn} = 0$ (the balanced bridge condition). Thus, in this section the linear effect prevails, although all of the three microwave fields are strong, and the bridge could act as a phase-

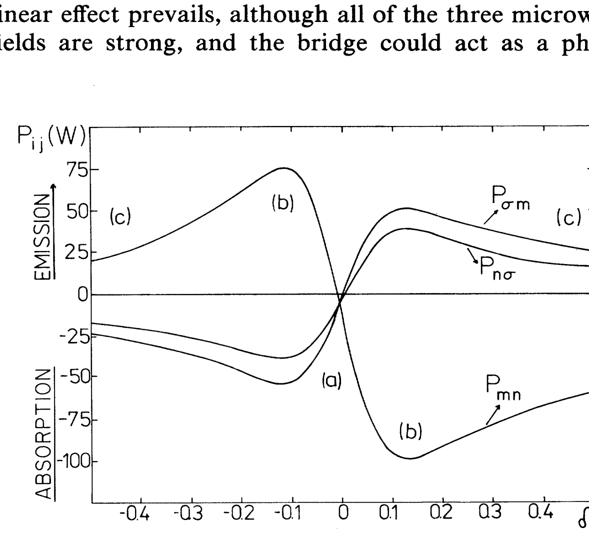

FIG. 2. The predicted dependences (Ref. 14) on δ of the absorbed or emitted powers P_{ij}.

sensitive detector.[12] In Figs. 1(b) and 2(b) (strong unbalanced bridge), $\delta_1 \ll |\delta_2| \cong |\delta| \ll 1$. In this case $\Omega_{mn} \cong \Omega_{n\sigma} \cong \Omega_{\sigma m} \gg |\Omega_{mn}^{n\sigma}|, |\Omega_{mn}^{\sigma m}|$, so that the heat absorbed by the lattice is low, the emitted power could be high, and since $P_{mn} \cong -(P_{n\sigma}+P_{\sigma m}) \gg P_L$, the efficiency η of the microwave generation could be unusually high.[12] However, as δ_1 are positive and never zero, $\eta < 1$. The greater (δ/δ_1) is, the higher the emitting powers and efficiency are. Thus, although Figs. 1(b) and 2(b) exhibit important nonlinear effects, the emitted powers are not saturated since in this case $P_{ij} \sim \langle p_{ij}^2 \rangle^{(1/2)}$, and not independent of $\langle p_{ij}^2 \rangle$ as in the case of one or two strong fields.

In Figs. 1(c) and 2(c) δ becomes considerably larger, and the contributions of the terms proportional to δ^2 and δ^3 for Δ prevail. In this case $\rho_{mm}-\rho_{nn}$ and P_{ij} decrease monotonically towards small values, while P_L increases towards its maximum (see Figs. 1 and 2). Thus, the usual cases of two strong fields [see Figs. 1(c) and 2(c) on the left side of the figures, where $\langle p_{n\sigma}^2 \rangle = \langle p_{\sigma m}^2 \rangle \gg \langle p_{mn}^2 \rangle$], or of a single strong field [see Figs. 1(c) and 2(c) on the right side of the figures where $\langle p_{mn}^2 \rangle \gg \langle p_{n\sigma}^2 \rangle, \langle p_{\sigma m}^2 \rangle$] could be considered particular cases of three frequency-correlated fields, when one or two among these fields are weak or vanishing.

V. CONCLUDING REMARKS AND OUTLOOK

The main differences between the maser action corresponding to three frequency-correlated fields when all the spectroscopic bridge conditions are fulfilled, and that corresponding to the usual cases of two fields are:

(i) While in the case of two fields, when both the saturating and emitted fields are strong, the nonlinear effects prevail, for balanced spectroscopic bridge [see Figs. 1(a) and 2(a)], although the three fields are strong, important linear effects occur. The higher intensities of the fields are, the stronger linear effects are. In addition, these linear effects allow a more sensitive detection.

(ii) When the spectroscopic bridge is strongly unbalanced [see Figs. 1(b) and 2(b)], although the nonlinear effects prevail, the saturating effects do not occur. This fact makes possible high emitting powers, generated with an unusually high efficiency.

There are also many other advantages of the method discussed here,[4,12] as compared to the usual maser action, e.g., the frequency of the emitted field may be higher than those of the pumping fields, the maximum efficiency of the generations or of the phase-sensitive detection is reached at optimum temperatures which are relatively high and which do not differ too much, and so on.

In order to obtain such performances as those mentioned above, besides the spectroscopic bridge conditions which have to be satisfied, the inhomogeneous broadening mechanisms have to be negligible. An example of such system which might fulfill all these conditions could be the S electron ions, like Pb^{3+} in calcite.[4,8]

The treatment summarized in this paper could be valid for any kind of multilevel system including the usual cases when the electric field contributes to p_{ij}, but only when all the spectroscopic bridge conditions are satisfied. Unfortunately, in the schemes proposed up to now, some of these conditions cannot be fulfilled.[1,13]

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