PHYSICAL REVIEW A VOLUME 14, NUMBER 5 NOVEMBER 1976

Atomic correlations and line shape in microwave second-harmonic generation*

R. Boscaino
Istituto di Fisica dell'Università, Palermo, Italy
and Gruppo Nazionale Struttura della Materia, Roma, Italy
(Received 14 May 1976)

Second-harmonic (SH) generation by paramagnetic samples at microwave frequency is considered, and the dependence of its intensity on the total number N of active centers is experimentally investigated. The reported results show a N^2 dependence of the SH intensity near the resonance condition and a higher N dependence in the far wings of the SH line. A qualitative explanation is suggested in which the observed effect is related to the internal correlations established among the spins during the SH generation process, as theoretically investigated in the following paper by Persico.

I. INTRODUCTION

It is well known that the interaction processes between light and matter are influenced to a large extent by internal correlations among the scattering or radiating centers. A well-known example is the super-radiance effect, first introduced by Dicke,[1] in the spontaneous emission process. More recently, collective aspects of the radiation phenomena have been theoretically considered in connection with several nonlinear interaction processes, such as Raman scattering, double quantum transitions, parametric amplification, and frequency conversion.[2-5] It has been shown that the probability of these processes is enhanced when some degree of atomic correlation is present, the enhancement factor being dependent on N, the total number of active centers. However, in practical cases, the correlations among the centers are counteracted by the dephasing agents, always present in every physical system, as relaxation interactions among the centers or with a thermal bath. Then the experimental detection of correlation effects in the radiation phenomena is expected to be limited to those situations where the characteristic time of the radiation process is shorter than the dephasing time. The interplay between correlation effects and dephasing agents should result in a higher or lower N dependence of the scattering cross section for the particular process under consideration. The N dependence can be taken, in turn, as a measure of the degree of internal correlation which a physical system is able to maintain in its response to an electromagnetic field.

In this paper the N dependence is experimentally investigated for a simple case of a nonlinear process, the second harmonic (SH) generation by a paramagnetic system of N two-level spins. As previously reported,[6] when such a system, tuned by an external magnetic field H_0, is irradiated with high power at frequency ω, a frequency conversion process takes place and a SH output at frequency 2ω can be detected. The phenomenon is resonant at fields H_0 such that $\gamma H_0 \equiv \omega_0 = \omega$ or $\omega_0 = 2\omega$, lending itself to an interpretation in terms of absorption of two photons of frequency ω and emission of a single photon of frequency 2ω, via intermediate states, some of them being virtual.

The experimental investigation of the degree of correlation among the spins in the SH generation process was originally stimulated by a discrepancy in the conclusions of two different theories which have been developed to explain the observed experimental results. One of them[6] is based on a density-matrix approach, in which the electromagnetic fields are treated classically and the relaxation times are introduced phenomenologically. The second[7] is purely quantum mechanical and the relaxation times are introduced only at the end, in order to allow a comparison with the experimental results. The results of the two theories agree, as far as the line shapes, the position of the lines, the dependence on the input power and the angular dependence are concerned. However, there is a remarkable difference between the two theories concerning the dependence of the SH intensity on the total number N of the spins, which is N^2 and, at least, N^3 for the semiclassical and the quantum-mechanical theory, respectively.

The disagreement in this respect is of a conceptual nature and is ascribed to the fact that correlations among the spins play a different role in the two approaches. In the density-matrix approach[6] a macroscopic magnetic moment oscillating at harmonic frequency is calculated, which depends linearly on N. Correlations among the spins are considered only in the final step, i.e., in the emission of the harmonic wave which is treated as a radiation by the oscillating magnetic moment, leading to a dependence of the SH intensity on N^2. Other correlations among the spins in the intermediate states cannot appear within this approach, as it involves thermal averages.[6] On the other hand, in the quantum-mechanical theory[7] the transition amplitude for the SH generation process is calculated and collective spin states are used throughout which are capable to take fully into account the correlations induced by the electromagnetic fields in each step of a multiphoton process; these correlations may indeed lead to a dependence of the emitted intensity on a power of N higher than 2.[7] It is therefore of interest to investigate which of the two approaches is appropriate to the physical situation.

In the following sections we report experimental results on the N dependence of the SH intensity, generated by a paramagnetic sample. It will be shown that some peculiarities of these results can hardly be explained without supposing that a correlation among the spins is established also in the intermediate state, i.e., in the double quantum absorption step. A suggestion for a qualitative and partial interpretation of the reported results will be briefly discussed. A more comprehensive account of all the experimental results will be presented in the following paper by Persico, in the framework of a new quantum-mechanical theory.

II. EXPERIMENTAL PROCEDURE AND RESULTS

The experimental apparatus used for the present measurements is essentially the same as the one reported in Ref. 6 and we refer to it for a detailed description. Here we wish only to specify the conditions in which the measurements have been performed, in order to make clear the discussion of the experimental results.

A bimodal microwave cavity was used resonating at $\omega = 2.7$ GHz in a partially coaxial mode and at $2\omega = 5.4$ GHz in its TE_{102} rectangular mode, with a relatively low quality factor, $Q \cong 400$ for both modes. The paramagnetic sample was located in a point of the cavity, where the magnetic fields $\vec{H}_\omega$ and $\vec{H}_{2\omega}$ of the two modes are maxima and orthogonal. Each sample, shaped in the form of a thin cylinder, was positioned in the cavity in such a way that its axis was perpendicular to the magnetic fields' plane: this shape and this orientation were recognized to minimize the effects coming from the nonuniformity of the microwave fields, for the particular geometry of the cavity. High power at the frequency $\omega = 2.7$ GHz was sent to the cavity to excite the ω mode, in the form of pulses lasting for $\simeq 2$ μsec and distant $\simeq 5$ msec. At the output of the receiver apparatus, appropriately tuned and calibrated, a voltage signal was detected, proportional to the power at 5.4 GHz that the paramagnetic sample radiated into the 2ω mode, because of the SH generation processes. The distance between the energy levels of the spin system was adjusted by adjusting the magnitude of the external static magnetic field $\vec{H}_0$. However rotated, $\vec{H}_0$ always was lying in the same plane of the microwave fields $\vec{H}_\omega$ and $\vec{H}_{2\omega}$, making an angle θ with $\vec{H}_{2\omega}$ and $\frac{1}{2}\pi - \theta$ with $\vec{H}_\omega$. In the following we take the direction of $\vec{H}_0$ as z axis and the magnetic fields' plane as zx plane. In this reference frame the cylindrical sample was aligned along the y axis, during the measurements. All the measurements were performed at liquid-helium temperature, $T = 4.2$ °K. As it has been reported[6] the SH intensity emitted by a paramagnetic sample is a function of the input power level as well as of the polarization angle θ. Unless otherwise indicated the measurements to be reported were taken at an angle $\theta = 50°$ and with a peak input power of 100 W: at this power level, the amplitude of the ω-oscillating field $\vec{H}_\omega$ at the sample position was estimated to be $\simeq 20$ G.

The investigation on the N dependence of the SH signal intensity has been performed on a set of eight samples of different weight of powdered DPPH (diphenyl picryl hydrazyl). The total number N of spins, derived from the weight, ranges from $N = 1.2 \times 10^{17}$ to $N = 1.9 \times 10^{19}$. The choice of DPPH among the paramagnetic materials was based on the consideration that correlations among the spins, in which we are interested, should be more easily maintained in samples with a long spin-spin relaxation time T_2: in DPPH the exchange interaction causes a lengthening of T_2 up to 6×10^{-8} sec in spite of the high concentration of spins.[8] Moreover, powdered DPPH samples exhibit a quite simple isotropic SH emission spectrum,[6] consisting of two lines, centered at $H_0 = 990$ G ($\omega = \omega_0$ line) and at $H_0 = 1980$ G ($\omega_0 = 2\omega$ line), respectively, at our frequencies. Near the $\omega_0 = \omega$ condition, the spin system is resonant with the input power and the analysis of the SH intensity measurements is entangled by the presence of saturation effects, which alter the shape of the line. For this reason, the experimental results reported below have been obtained on the $\omega_0 = 2\omega$ line.

First, the intensity at the maximum of the $\omega_0 = 2\omega$ line ($H_0 = H_{0_r} \equiv 1980$ G) was measured in the eight samples of DPPH. Reliability of these measurements was achieved by means of a reference sample, a ruby crystal ($Cr^{3+}:Al_2O_3$), placed in the cavity always in the same position and with its "c" axis aligned along the y axis. Each DPPH sample was placed in turn in the cavity and the maximum intensity of its SH line was measured relatively to the intensity of the SH line at $H_0 = 3850$ G of the ruby crystal. The results are reported in Fig. 1 as a function of N: by fitting with a power law N^α, we get $\alpha = 2.0 \pm 0.1$, in good agree-

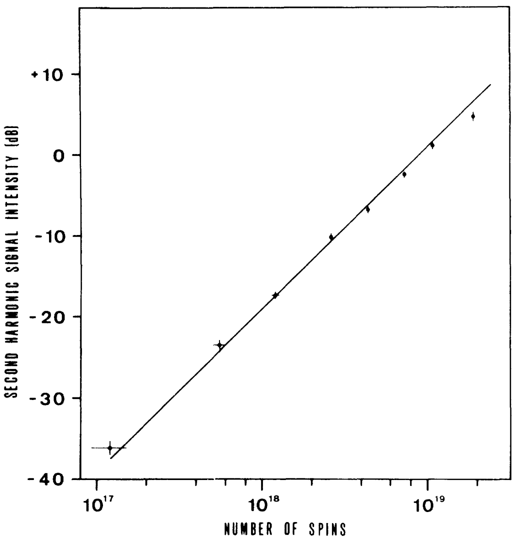

FIG. 1. Peak intensity of the $\omega_0 = 2\omega$ SH line as a function of the total number N of spins, for eight samples of concentrated DPPH. The intensity of the reference signal is taken as 0 dB level.

ment with the predictions of the semiclassical theory. The deviation from the square law which is observed in the largest of the samples ($N = 1.9 \times 10^{19}$) may be perhaps attributed to the reaction effect of the $\vec{H}_{2\omega}$ field, which will be discussed later. In order to ensure the absence of these spurious effects, this sample was not used in the measurements reported below.

More interesting results about the N dependence of the SH intensity were obtained, when the radiating spin systems were detuned from the exact resonance condition $\omega_0 = 2\omega$. In DPPH the width of the SH line, as measured at the half-power points, is only 3 G, but its Lorentzian shape and the high sensitivity of the SH spectrometer allow the measure of the intensity up to a detuning $\Delta H = H_0 - H_{0r} = 1000$ G for the largest of the samples. In Fig. 2 we report the wings of the SH line, as experimentally detected in some of the DPPH samples with different N. The reference sample could not be used when making these measurements, as the wings of its lines overlap the wings of interest: for each DPPH sample, the SH intensity in the wings was measured relatively to its center maximum at $\Delta H = 0$, previously calibrated. In Fig. 2, where each line is normalized to its own maximum (0 dB level), the SH line appears to have a N-dependent shape, as the wings tend to raise with respect to the center maximum in samples with large N. As a consequence, the N dependence of the SH intensity is different in the wings and at resonance. The same data are reported in a different display in Fig. 3, where the SH intensity, measured at particular values of ΔH and normalized to the maximum at $\Delta H = 0$, is plotted versus the number N of spins. By fitting the intensity data with a power law N^{α}, we get that, in the investigated range of N, the exponent α is a function of ΔH: α

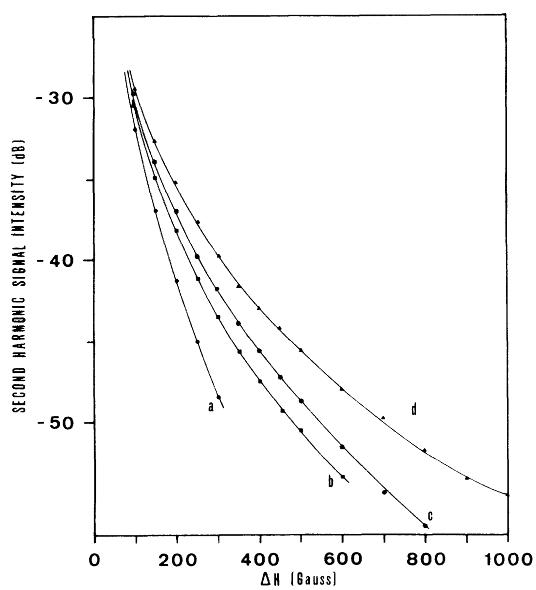

FIG. 2. Wings of the SH line as a function of $\Delta H = H_0 - H_{0r}$ for four different samples of DPPH: (a) $N = 5.5 \times 10^{17}$, (b) $N = 1.2 \times 10^{18}$, (c) $N = 2.6 \times 10^{18}$, (d) $N = 7.2 \times 10^{18}$. The intensity of each line is normalized to its own maximum at $\Delta H = 0$, taken as 0 dB level.

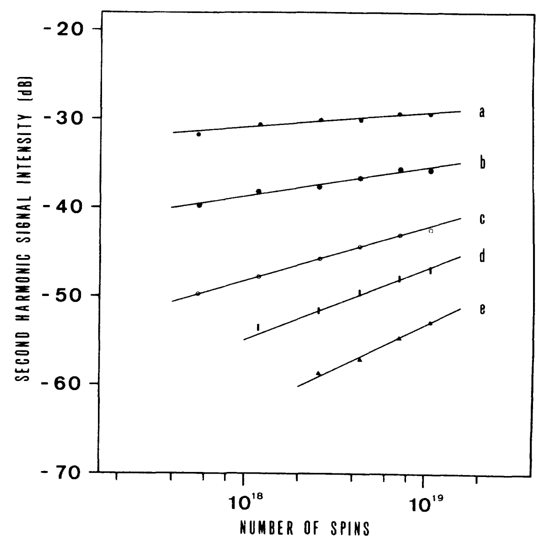

FIG. 3. SH intensity in the wings at different values of $\Delta H = H_0 - H_{0r}$ as a function of the total number N of spins for some samples of DPPH. (a) $\Delta H = 100$ G, $\alpha = 2.1$; (b) $\Delta H = 200$ G, $\alpha = 2.3$; (c) $\Delta H = 400$ G, $\alpha = 2.6$; (d) $\Delta H = 600$ G, $\alpha = 2.8$; (e) $\Delta H = 1000$ G, $\alpha = 3.0$. The SH intensity for each sample is normalized to its own maximum at $\Delta H = 0$.

is equal to 2.0 at resonance ($\Delta H = 0$), but increases on detuning the spins up to 3.0 at large values of ΔH.

The properties of the emitted SH power have been found to depend on the detuning of the spin system not only as far as the N dependence is concerned, but also with respect to the angular θ dependence. As it has been previously reported,[6] both a z component and an x component of the $\vec{H}_\omega$ field are required to produce the SH emission near the $\omega_0 = 2\omega$ condition, thus introducing a θ dependence of the radiated power. The experimental dependence on θ near the maximum of the line was reported to be well fitted by the function $\sin^4\theta \cos^2\theta$, in agreement with the theory.[6] In Fig. 4 the far wings of the SH line, as experimentally detected in the DPPH sample with $N = 7.2 \times 10^{18}$, are reported at some values of θ, each line being normalized to its own maximum: the raising of the wings, observed in samples with large N, appears in Fig. 4 to be a θ-dependent effect, being more pronounced at high-θ values. This dependence is evidenced in Fig. 5, in which the SH intensity at $\Delta H = 0$ and at $\Delta H = 500$ G is plotted versus the angle θ. While the intensity data at resonance are well fitted by the function $\sin^4\theta \cos^2\theta$ (continuous line in the figure), the data at $\Delta H = 500$ G shift toward a θ dependence, in which the exponent of the sine function is larger than 4.0.

Before concluding this section we wish to remark that the reported results are independent on the input power level. In fact the SH intensity has been checked to vary as P^2, where P is the input peak power, both at the maximum and in the wings. In addition, we have also examined the region $\Delta H < 0$ of the lines up to $\Delta H = -200$ G (measurements at larger values of $|\Delta H|$ on this side of the lines are not reliable, because of the wings of the $\omega_0 = \omega$ lines). We found that the raising of the wings in samples with large N is present also in the region $\Delta H < 0$ and in the same way as for $\Delta H > 0$. These facts rule out the possibility that the reported change in the line shape could be ascribed to high-power effects, such as saturation broadening and heating or cooling of some other energy reservoir,[9] which are typical causes of change of the shape of the usual first-order absorption line.

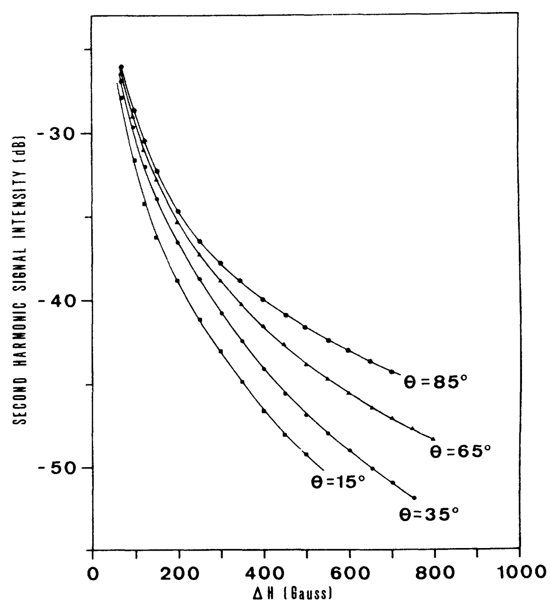

FIG. 4. Wings of the SH line $\omega_0 = 2\omega$ of the DPPH sample with $N = 7.2 \times 10^{18}$ at various values of the polarization angle θ. At each value of θ, SH intensity is normalized to the maximum value at $\Delta H = 0$, taken as 0 dB level.

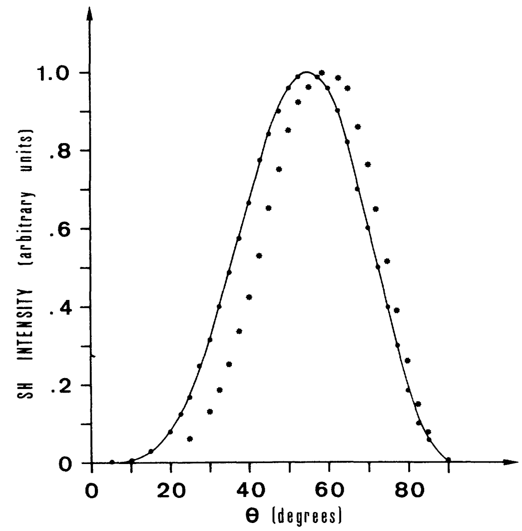

FIG. 5. SH intensity as a function of the angle θ in the DPPH sample with $N = 7.2 \times 10^{18}$ at $\Delta H = 0$ (dots) and at $\Delta H = 500$ G (stars), in arbitrary units. The continuous line is a plot of the function $\sin^4\theta \cos^2\theta$ normalized to 1.0.

III. DISCUSSION

In the following we examine the possibility of explaining the reported results in the framework of the semiclassical theory, i.e., without supposing any correlation among the spins apart from the final step of the SH generation process.

According to the density-matrix calculations,[6] the nonlinear 2ω-oscillating magnetization $M_{2\omega}^{\mathrm{NL}x}$ near $\omega_0 = 2\omega$ has an amplitude given by

$$M_{2\omega}^{\mathrm{NL}x} = (H_\omega^x H_\omega^z / H_0)\chi^{\mathrm{LIN}}(\omega_0). \tag{1}$$

H_ω^x and H_ω^z are the x and z components of $\vec{H}_\omega$ and $\chi^{\mathrm{LIN}}(\omega_0)$ is the complex first-order magnetic susceptibility of the sample, calculated at the frequency 2ω: Eq. (1) is the same as Eq. (13) of Ref. 6 with

$$\chi^{\mathrm{LIN}}(\omega_0)=\tfrac{1}{2}\chi_0\omega_0T_2\frac{(2\omega-\omega_0)T_2-i}{(2\omega-\omega_0)^2T_2^2+1}\ , \qquad (2)$$

where χ_0 is the static magnetic susceptibility, T_2 is the spin-spin relaxation time, and i the imaginary unit. According to Eq. (1), the reported N-dependent raising of the wings in the SH line should be related to a similar property of $\chi^{\mathrm{LIN}}(\omega_0)$, which is the first-order response function: then the same effect should be observable when detecting the usual EPR (electron paramagnetic resonance) line shape, which is proportional to $\chi^{\mathrm{LIN}}(\omega_0)$. Indeed, EPR absorption lines which depend on the shape and the volume of the sample are observed when the resonant spin system is embedded in a (electronic or nuclear) paramagnetic matrix, because of the effects of the demagnetization coefficients.[10] However, experimental evidence against this explanation of our results is found when considering the θ dependence reported in Fig. 3 and the geometry of our experiments. In fact the powder structure and the shape of the used samples ensure complete symmetry around the y axis, as defined above: the shape of $\chi^{\mathrm{LIN}}(\omega_0)$ must be strictly insensitive to any rotation of H_0 in the xz plane. So the reported raising of the SH wings can hardly be considered a property of the first-order response function. Rather, it appears to be a peculiarity of the SH generation process, which cannot be explained on the basis of Eq. (1).

We can try to improve Eq. (1), by taking into account the reaction of the 2ω-oscillating field on the spin system. In fact the 2ω-oscillating magnetization of the sample is the sum of two contributions:

$$M_{2\omega}^{x}=M_{2\omega}^{\mathrm{NL}\,x}+M_{2\omega}^{\mathrm{LIN}\,x}, \qquad (3)$$

where $M_{2\omega}^{\mathrm{NL}x}$, defined by Eq. (1), is the term caused by nonlinear effects, while M^{LIN},

$$M_{2\omega}^{\mathrm{LIN}x}=H_{2\omega}^{x}\chi^{\mathrm{LIN}}(\omega_0), \qquad (4)$$

is a reaction term caused by the 2ω-oscillating field $\vec{\mathrm{H}}_{2\omega}$ in the cavity. According to the normal mode theory for resonant cavities

$$H_{2\omega}^{x}=-4\pi i\eta QM_{2\omega}^{x}\ , \qquad (5)$$

where $i=\sqrt{-1}$, η is the filling factor of the sample in the 2ω mode of the cavity, and Q is the quality factor. By substitution one gets

$$H_{2\omega}^{x}=\frac{-1}{1+4\pi iQ_{\eta}\chi^{\mathrm{LIN}}(\omega_0)}M_{2\omega}^{\mathrm{NL}x}4\pi iQ\eta. \qquad (6)$$

The detected SH signal is proportional to $|H_{2\omega}^{x}|^2$. In Eq. (6) a correction factor appears which, depending on η, is able to change the shape of the SH line in an N-dependent fashion. However, in Eq. (6) the effect of the correction factor is to lower the N dependence of the SH signal at the center of the line, where $\chi^{\mathrm{LIN}}(\omega_0)$ is maximum, while its contribution is negligible in the far wings. On the contrary, the experimental results reported in Fig. 1 show a N^2 dependence at the center of the SH line for all the samples except for the largest one. This sample is probably the only one for which this reaction effect plays a role and for this reason it has not been used for the measurements in the wings. More exactly, with the parameters of the cavity and for all the samples used except the largest one, we estimated that the effect of the field reaction is to lower the SH intensity of 0.8 dB in the less favorable case. Consequently, at least as far as the experimental results reported in Sec. II are concerned, this effect can be neglected to a good approximation.

On the basis of the above considerations we are driven to relate the higher-than-square N dependence observed in the wings of the SH line, to the degree of correlation with which the spin system evolves under the action of the electromagnetic fields. According to the reported results, the degree of internal correlation among the spins in the SH generation process is different at resonance and off resonance. Near the resonance condition the properties of the SH wave and the spin dynamics are well described by a density-matrix approach. As remarked above, this means that the spins behave in a correlated way only in the emission of the 2ω quanta. In this picture the spin-spin interactions should be effective in breaking the correlations established among the spins during the first steps of the process and the thermal averages involved in the density-matrix calculations may be expected to be a good approximation. On the contrary, the extra N dependence observed when the spins are off resonance has to be taken as the experimental evidence of the cooperative effects predicted by the quantum mechanical theory.[7] In other words, experimental results seem to confirm that when the spins are driven far from resonance, the internal correlations established during the double quantum absorption are maintained up to the end of the SH generation process, thus influencing the properties of the emitted SH power. We are led to conclude that, with respect to the intermediate step of the process, a gradual transition takes place from a single-spin behavior to a collective one, as the spins are more and more detuned out of the resonance.

A hint for a qualitative understanding of the observed change in the spins behavior is given by considering the lifetime of the intermediate state and its dependence on the detuning of the spin system $\Delta = \omega_0 - 2\omega$. This problem has recently attracted the attention of many authors, in connection with the near-resonant Raman scattering.[11-13] Experimental evidence has been given that the lifetime t^* decreases and tends to zero, as the intermediate state is moved away from an energy-conserving real state.[13] In a similar way, in our case, when the resonance condition is not satisfied, the double quantum absorption does not conserve the energy of the system (spins $+\omega$ photons) and the lifetime t^* of the virtual intermediate state in which the system is left, is expected to be a decreasing function of Δ. During the time t^* the system is exposed to the action of the relaxation interactions which tend to destroy the coherence among the spins. As Δ is increased, because of the decreased t^*, the system tends to become insensitive to the dephasing agents and to preserve the internal correlations. In this limit the behavior predicted by the quantum-mechanical theory[7] should be expected, with a N^4 dependence of the SH intensity. On the contrary, when going toward the resonance condition, because of the increased t^*, the dephasing agents have enough time to impose a single-spin behavior, thus yielding a N^2 dependence of the SH intensity.

It is not easy only on the basis of this simple argument to account for the angular dependence reported in the Figs. 4 and 5. In the following paper by Persico a quantum-mechanical theory using collective spin states and taking into proper consideration the relaxation interactions is developed and we refer to it for a more quantitative discussion of all the reported results on the N dependence of the SH intensity and its variation with the angle θ.

ACKNOWLEDGMENTS

We wish to acknowledge very frequent and helpful discussions with F. Persico, whose theoretical work has been a continuous stimulus for the experiments reported here. We wish also to thank M. W. P. Strandberg and I. S. Ciccarello for useful suggestions.

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*Partial general support was also provided by the Comitato Regionale Ricerche Nucleari Struttura della Materia, Palermo, Italy.

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