Anomalous rate of free-induction decay

R. Boscaino and V. M. La Bella
Istituto di Fisica, Università degli Studi, Via Archirafi 36, I-90123 Palermo, Italy
(Received 4 December 1989)

The steady-state free-induction decay (FID) has been investigated in samples of crystalline and amorphous quartz containing paramagnetic two-level electron spin centers ($S=\frac{1}{2}$). We report experimental data on the dependence of the FID rate on the Rabi frequency χ induced during the preparative stage. Our results confirm that the decay of the FID signal is much slower than expected on the basis of the conventional Bloch equations. The range of χ investigated here is wide enough to show the whole transition from Bloch-type behavior to the high-power Redfield limit, in which the FID rate is determined only by χ. The experimental data are compared with theoretical results recently obtained by hypothesizing Gaussian-Markovian fluctuations of the resonance frequency. Even if agreement is poor, the comparison suggests by itself the possibility that more than one source of fluctuations may be effective. Other possible origins of the failure of the Bloch equations as well as of the stochastic theories are examined.

I. INTRODUCTION

The conventional Bloch equations (BE) provide a simple description of the resonance dynamics of two-level systems in an e.m. field, both in magnetic resonance and in optics.[1] In these equations the generic center (atom or spin) has a time-independent frequency ω_{0i} and its relaxation dynamics is described in terms of two parameters, the longitudinal T_1 and the transverse T_2 relaxation times. Since the earliest studies of magnetic resonance,[2,3] situations have been known in which the phenomenological Bloch model fails to account for the observed responses, especially in solids ($T_1 \gg T_2$) and in the presence of a strong field.[4,5] This failure may have several origins. First, the homogeneous contribution to the resonance broadening may be non-Lorentzian. Second, the resonance frequencies ω_{0i} may fluctuate in a time scale comparable with the observational one. Moreover, the microscopic relaxation mechanisms may be influenced by the incoming radiation. Finally, for an inhomogeneously broadened line, intraline spectral-diffusion mechanisms (not allowed for by the BE) may play a relevant role.

More recently, departures from the behavior predicted by the BE have been experimentally observed and theoretically investigated in connection with free-induction decay[6–8] (FID), hole-burning,[9] decay of nutational regime,[10] and echo.[11] In particular, as regards the FID effect, namely, the emission of radiation ensuing the abrupt interruption of the pump field, it has been observed[6–8] that the FID emission in solid systems at low temperature ($T_1 \gg T_2$) decays much more slowly than predicted by the BE. The observations of anomalous FID have stimulated much theoretical work[12–19] in which the non-Bloch power dependence of the FID rate has been ascribed to the fluctuations of the resonance frequency ω_{0i} of the single active center. In these theories the fluctuations of ω_{0i}, responsible for the coherence loss in the weak-field limit, are shown to become uneffective in a strong field. The calculated FID rate Γ tends to the value $\Gamma=2/T_2$ in the low-power limit, in agreement with the Bloch model, and to the value $\Gamma=\chi/\sqrt{2}$ in the opposite limit of strong fields (the field intensity is usually measured in terms of the induced Rabi frequency χ). In the intermediate power range the FID behavior is determined by the particular stochastic model assumed for $\omega_{0i}(t)$. So, the power dependence of Γ has been given most attention when comparing experimental and theoretical results obtained by hypothesizing several kinds of stochastic processes for $\omega_{0i}(t)$.

A quantitative and consistent account of the experimental results of the χ dependence of Γ has not been given by the models developed until the present time. Even if agreement has been found for limited ranges of the radiation intensity, the best fitting value of the correlation time τ_c of $\omega_{0i}(t)$ is often conflicting with the T_2 value or with the single-exponential form of experimental FID signals.[16] The circumstance that the range of χ investigated experimentally up to now is somewhat limited and the large scattering of the experimental data make more difficult a reliable comparison with theories and the need for additional experiments has often been claimed.[16,17] Other problematic aspects of the FID emission concern as well the low- and the high-power regimes. In fact, the question has been raised whether the low-power FID behavior and the echo experiments should be expected to yield the same value of T_2.[16] On the other hand, it has to be noted that the existence of the high-power limit ($\Gamma=\chi/\sqrt{2}$) implies that the rapid Rabi flipping is capable of suppressing the effects not only of the frequency fluctuations, but also of any other dephasing mechanism effective in the unperturbed system.

In this paper we report experimental data on the shape and rate of the FID signal in systems of $S=\frac{1}{2}$ spins diluted in solid matrices at low temperature. A peculiarity of the experiments reported here is the wide range of χ (nearly two decades) investigated; moreover, data scattering is much reduced with respect to previous reports by using nonlinear spectroscopy techniques. In the whole investigated range of χ, from the validity zone of the BE to the high-power limit, we have observed that the FID signal has a single-exponential shape over a wide excursion (nearly 25 dB) with a power-dependent decay rate Γ. Our data on the dependence of Γ on χ are compared here with the theoretical results obtained[12,13] by hypothesizing a Gaussian-Markov process for $\omega_{0i}(t)$. Even if we do not find agreement, the comparison suggests by itself that more than one fluctuation mechanism with different τ_c may be effective. Other possible origins of the failure of the BE as well as of the stochastic theories are examined.

The paper is organized as follows. In Sec. II we briefly recall the properties of the FID signal as calculated from the BE and we examine the Redfield limit. Sec. III is devoted to experiments and the results are compared with the stochastic theories in Sec. IV. In Sec. V we discuss possible origins of the failure of BE and stochastic theories.

II. THE BE SOLUTIONS AND THE REDFIELD LIMIT

We briefly recall the main properties of the FID signal emitted by an ideal inhomogeneous system obeying the conventional BE. We consider a system of N spins $S=\frac{1}{2}$ whose frequencies ω_{0i} are distributed about a mean value ω_0 according to a Gaussian $h(\omega_{0i}-\omega_0)$ with a standard deviation σ. At this moment we assume that (i) the frequencies ω_{0i} are time independent (static inhomogeneous broadening) (ii) the interaction between spins having different ω_{0i} can be disregarded, and (iii) each isochromat obeys the BE, all with the same relaxation times T_1 and T_2. This is by far the simplest picture of an inhomogeneous line.[20]

During the preparative stage ($t<0$) a microwave magnetic field $\mathbf{b}(t)=2\mathbf{b}_1\hat{\mathbf{x}}\cos(\omega t)$ perpendicular to the static field $\mathbf{B}=B\hat{\mathbf{z}}$ and tuned to the resonance $\omega=\omega_0$ saturates the system. In the rotating reference frame (RRF), within the rotating-wave approximation, the generic spin packet, detuned by $\epsilon=\omega_{0i}-\omega_0$ from the line center and then from the input radiation, is characterized by a steady-state vector (u,v,w):

$$u(\epsilon)=\epsilon\chi T_2^2/D \;, \tag{1a}$$

$$v(\epsilon)=-\chi T_2/D \;, \tag{1b}$$

$$w(\epsilon)=(1+\epsilon^2T_2^2)/D \;, \tag{1c}$$

with $D=1+\epsilon^2T_2^2+\chi^2T_1T_2$. Here u, v, and w are the components of the spin-packet magnetization (normalized to the thermal equilibrium value M_0), $\chi=\gamma_G b_1$ is the Rabi frequency, and γ_G is the gyromagnetic ratio.

When the field is switched off at $t=0$, each spin packet precesses in the RRF at frequency ϵ damped by the relaxation interactions. For $T_2 \ll T_1$ (as usual in low-temperature solids) and in a time scale of the order of T_2, the time evolution of the generic packet is given by

$$u(\epsilon,t)=-v(\epsilon)\exp(-t/T_2)[\epsilon T_2\cos(\epsilon t)+\sin(\epsilon t)] \;, \tag{2a}$$

$$v(\epsilon,t)=v(\epsilon)\exp(-t/T_2)[\cos(\epsilon t)-\epsilon T_2\sin(\epsilon t)] \;, \tag{2b}$$

and $w(\epsilon,t)\simeq w(\epsilon)$. The transient regime of the whole system $[U(t),V(t),W(t)]$ is obtained by integrating the above solutions over $h(\epsilon)$. One gets[21] $U(t)=0$ and

$$V(t)=(\pi^{1/2}/2\sigma T_2)(\chi/\gamma)\exp(-t/T_2)K(t) \tag{3}$$

with

$$K(t)=\exp[(\gamma/\sigma)^2][(\gamma T_2-1)\exp(-\gamma t)\mathrm{erfc}(y_1) - (\gamma T_2+1)\exp(\gamma t)\mathrm{erfc}(y_2)] \;, \tag{4}$$

$$\gamma=(1/T_2)(1+\chi^2T_1T_2)^{1/2} \;. \tag{5}$$

Here $y_1=\gamma/\sigma-\sigma t/2$, $y_2=\gamma/\sigma+\sigma t/2$, and $\mathrm{erfc}(y)$ is the complementary error function.[22] In the laboratory reference frame (LRF), for $t>0$ the system exhibits a transverse magnetization $[M_x(t)+iM_y(t)] = M_0V(t)\exp(i\omega_0 t)$ that emits radiation at frequency ω_0 with a time-dependent intensity $I(t)\propto[V(t)]^2$ (FID emission).

The exponential damping term in Eq. (3) is an irreversible contribution to the decay of $V(t)$, due to the coherence loss of the individual packets *during* the FID regime; its exponential form as well as the Lorentzian shape of the spin-packet line is a consequence of the particular expression of the relaxation terms in the BE. On the other hand, $K(t)$ in Eq. (3) yields an additional (reversible) time dependence of $V(t)$, due to the superposition of the oscillations at different frequencies; $K(t)$ is a consequence of the inhomogeneous broadening and it depends on the steady-state properties of the system during the preparative stage; in fact, physically γ represents the spectral width of the saturated packet line. Approximate expressions of $K(t)$ can be obtained[21] if the resonance line is highly inhomogeneous ($\sigma T_2 \gg 1$) and poor saturation of the overall line ($\gamma/\sigma \ll 1$) is induced:

$$K(t)\simeq K(0)+\gamma\sigma T_2[2\pi^{-1/2}+K(0)\gamma/\sigma]t \tag{6}$$

at short times $t \ll (2\chi/\sigma^2T_2)(T_1/T_2)^{1/2}$ and

$$K(t)\simeq 2(\gamma T_2-1)\exp(-\gamma t) \tag{7}$$

at long times $t\gg\sigma^{-1}$. Equation (6) shows that immediately after removing the field a sort of rephasing of the packets occurs and yields a rapid growth of the transverse magnetization of the whole system (often referred to as *linear* FID regime);[21] as this growth occurs in a time scale shorter than our observational one, it will not be considered here. In a longer time scale $t\gg\sigma^{-1}$ (*nonlinear* FID regime) $K(t)$ [Eq. (7)] yields an additional exponential damping of $V(t)$:

$$V(t)=\pi^{1/2}(\chi/\gamma)[(\gamma T_2-1)/\gamma T_2]\exp(-\Gamma t) \tag{8}$$

with

$$\Gamma=1/T_2+\gamma=1/T_2)[1+(1+\chi^2T_1T_2)^{1/2}] \;. \tag{9}$$

Note that within the approximations used to get Eq. (7) the reversible contribution to the decay of $V(t)$ directly images the saturated steady state, being merely the Fourier transform of the saturated spin-packet line shape

[Eq. (1b)]. The possibility of investigating the saturation behavior of the system by monitoring the FID emission relies on this relationship. In fact, any departure of the actual steady state from the Bloch model predictions is expected to result in a χ dependence of Γ different from Eq. (9).

Finally we examine the high-power limit of the Redfield theory.[2] According to this model, the transverse relaxation of a saturated spin system should be described by an effective intensity-dependent T_{2e} lengthening from its low-power value T_2 to $T_{2e}=2T_1$ in the very-high-power limit. So, posing $T_2=T_{2e}=2T_1$ in Eq. (9), we get the high-power asymptotic behavior of Γ

$$\Gamma_R=\chi/\sqrt{2} \tag{10}$$

where the label denotes the high-power limit of the Redfield theory. We recall that the Redfield theory is concerned with an homogeneous system in which the main dephasing source is the dipolar coupling among the center. Explicit functional dependence of T_{2e} on the field intensities in the intermediate range have been theoretically calculated and experimentally investigated.[3,5]

In Sec. III we report measurements of the FID rate Γ as a function of χ and Eqs. (9) and (10) (henceforth referred to as Bloch and Redfield limit) will be used as touchstones of the experimental results.

III. EXPERIMENTS

A. The samples

We have observed anomalous FID signals in several samples, including E' centers in silica, $[AlO_4]^0$ centers in quartz, dilute ruby (Cr^{3+}:AL_2O_3), Ce^{3+}:$CaWO_4$. Here we report the results obtained in two samples of quartz containing $[AlO_4]^0$ centers[23] with different concentration (samples No. 1 and No. 2) and one sample of E' centers[24] in glassy silica (sample No. 3), as listed in Table I. Both kinds of centers were obtained by γ irradiating the samples in a ^{60}Co source at room temperature with a typical dose of 1000 Mrad. The different concentration of centers in samples No. 1 and No. 2 is due to the different content of Al impurities in the original nonirradiated samples.

$[AlO_4]^0$ centers[23] in crystalline quartz are hole defects ($S=\frac{1}{2}$) created by γ rays near Al impurities. Their resonance spectrum consists of six well-resolved lines separated by 0.6 mT due to the hyperfine interaction with the nuclear spin $I=\frac{5}{2}$ of ^{27}Al nuclei. Each hyperfine line has an inhomogeneous width of nearly 0.1 mT. The measurements reported here were taken at the center of the high-field line; however, similar results were obtained as well on the other lines.

E' centers[24] are hole defects ($S=\frac{1}{2}$) created by γ rays near an oxygen vacation. In a glassy matrix their resonance line is inhomogeneously broadened with a width of nearly 0.2 mT. Due to the high purity of the original piece of silica, no other absorption line of ionized impurities was observed in this sample after γ irradiation.

These samples were chosen for their relatively long relaxation times at low temperature ($T=4.2$ K); the values of T_1 and T_2 of our samples, measured by standard techniques (spin-echo and saturation-recovery) in the same conditions as for the FID measurements ($B=0.2$ T, $T=4.2$ K), are listed in Table I. In this regard we report that in all the samples and conditions explored, the experimental echo-decay curves were found to be well fitted by a single-exponential law.

TABLE I. Samples and their relaxation times in our working conditions ($B=0.2$ T, $T=4.2$ K).

Sample no.	Centers	Matrix	T_2 (μs)	T_1 (ms)
1	$[AlO_4]^0$	quartz	75±8	5.0±0.8
2	$[AlO_4]^0$	quartz	600±50	45±5
3	E'	silica	115±10	200±30

B. Method and apparatus

As a general scheme, a FID experiment consists of a preparative stage, during which the system is driven to a saturated steady state by a long pulse of resonant radiation and of a detection stage in which one monitors the radiation emitted by the system after removing the field. A peculiarity of our experimental procedure is that the preparative stage is accomplished by means of two-photon (TP) transitions.[7,25] In our experiments, during the preparative stage the system is driven by a microwave field $\mathbf{b}=2\mathbf{b}_1\cos(\omega t)$ polarized at an angle α with respect to the z-directed static field $\mathbf{B}$, $\mathbf{b}_1=b_1\cos\alpha\hat{\mathbf{z}}+b_1\sin(\alpha)\hat{\mathbf{x}}$. When $\mathbf{B}$ is adjusted to tune the system frequency ω_0 to the TP resonance $\omega_0=2\omega$, owing to the presence of both a longitudinal and a transverse component of $\mathbf{b}(t)$, TP transitions between the upper and lower levels of each spin center are allowed,[26] which induce saturation and establish a transverse coherence analogous to the one-photon resonance case. The detection stage is performed in a standard way: After switching off the field, we detect the radiation emitted by the system in a narrow spectral band centered at ω_0. It is worth pointing out that by this procedure we detect one-photon FID and that TP transitions are used only to establish the steady state. As $\omega_0=2\omega$, our experimental configuration is often referred to as a TP-induced second-harmonic (SH) FID experiment.[7] The advantages of this procedure are related to the large spectral distance between the exciting field and the system response and have been thoroughly discussed in connection with several coherent transient experiments.[25,27] Here we limit ourselves to recall that all the considerations stated in Sec. II can be generalized in a straightforward way to our TP-excited FID experiment. In fact, as previously shown,[27,28] in a properly defined double-rotating reference frame (DRRF) the steady-state response of a $S=\frac{1}{2}$ spin system for $\omega_0=2\omega$ is given just by the same Eq. (1) provided that χ is given the meaning of TP-Rabi frequency:[28,29] $\chi=-(\gamma b_1)^2\sin(2\alpha)/\omega_0$. After switching off the pump field, the transverse coherence $V(t)$ in DRRF manifests itself in the laboratory frame as a transverse magnetization oscillating at ω_0 with the time-dependent amplitude $V(t)$ given by Eq. (3).

In the experimental apparatus the sample is located in a bimodal cavity resonating at $\omega_1 = 2\pi 2.95$ GHz (pump mode) and at $\omega_2 = 5.9$ GHz (detection mode) in a point of the cavity where it is coupled to both modes. Both modes have a relatively low quality factor, with a half width of nearly 0.6 MHz. Fine tuning of the detection mode to $\omega_2 = 2\omega_1$ is obtained by inserting a quartz rod. The output signal of a low-power cw microwave source, tuned to the pump mode ($\omega = \omega_{c1}$), is first pulse shaped by a fast modulator (nominal transition time: 20 ns), then raised to the required power level (0.1–20 W) by a traveling-wave tube amplifier, and finally sent to feed the pump mode. By a superheterodyne receiver we monitor the time-dependent microwave signal emitted by the spin system into the monitor mode of the cavity after the trailing edge of the pump-field pulse. Two different receivers have been used for the measurements reported below. For the measurements taken at high input power, when a fast-decaying FID signal was emitted, we used a receiver whose i.f. amplifier has a bandwidth (BW) of 10 MHz; for the measurements taken at low power, when the FID signal has low intensity and decays slowly, in order to improve the signal-to-noise ratio (S/N), we used a receiver (actually, a spectrum analyzer working in its receiver mode) whose i.f. amplifier has a BW adjustable from 0.3 to 3.0 MHz. Both receivers output a logarithmic video signal, calibrated with the accuracy of ± 0.2 dB, which is sent to a digital transient recorder (time resolution: 0.2 μs). Further improvement of the S/N ratio is required and accomplished by averaging over a number of pulses, typically 256. Obviously, the repetition frequency f is low enough (typically 1 Hz) as to ensure complete

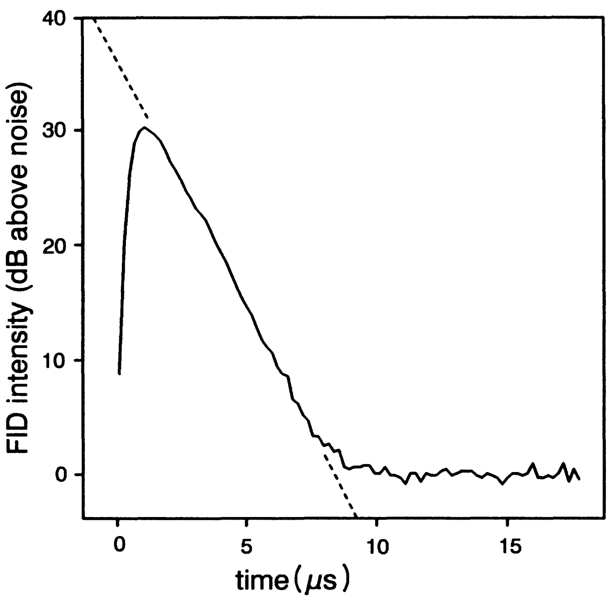

FIG. 1. A typical experimental curve of the FID signal. The curve was detected in sample No. 1 after a preparative stage ($t<0$) performed by a radiation pulse lasting 1 ms and including a Rabi frequency $\chi/2\pi = 54$ kHz. The dashed line is the exponential law $y = [A \exp(-\Gamma t)]$ with $\Gamma = 2\pi 78$ kHz, that best fits the decay part of the experimental curve.

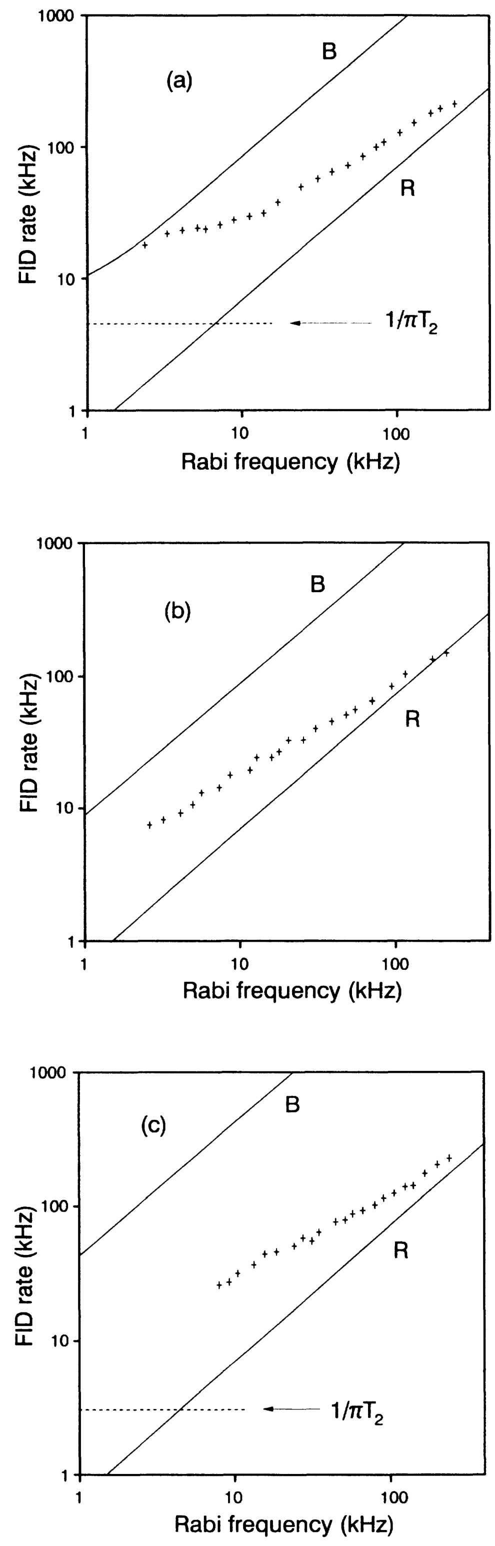

FIG. 2. Experimental dependence of the FID rate $\Gamma/2\pi$ on the Rabi frequency $\chi/2\pi$, as detected in our samples No. 1 (a), No. 2 (b), and No. 3 (c). For the sake of clarity, only a selection of the measured data has been reported. The solid lines marked B and R plot the theoretical dependences expected from the Bloch theory (B) [Eq. (9)] and from the Redfield one (R) [Eq. (10)]. The dashed lines mark the limit of the Bloch curve (B) for $\chi = 0$: (a) 4.2 kHz; (b) 0.53 kHz (out of scale); (c) 2.8 kHz.

TABLE II. Relevant parameters in FID experiments. Values and investigated ranges in our work and in previous reports.

Quantity	Pr^{3+}:LaF_3 (Ref. 6)	Cr^{3+}:Al_2O_3 (Ref. 8)	Our samples No. 1	No. 2	No. 3
$(T_1T_2)^{1/2}$ (10^{-4} s)	1.0	2.5	0.6	52	48
$\chi/2\pi$ (kHz)	2.0/40	8.5/85		3.0/200	
$\chi^2T_1T_2$	1.7/680	0.2/20	0.01/60 $\times 10^4$	0.01/40 $\times 10^6$	0.01/40 $\times 10^6$
χT_2	0.3/5.5	0.75/7.4	1.5/95	12.5/750	16/145
$\gamma/2\pi$ (kHz)	10/40	13/40		15/260	

thermal relaxation of the spin system between successive pulses ($fT_1 \ll 1$). The repetitive operation, the acquisition, the average and storage for further off-line analysis, is accomplished under the control of a microcomputer system.

C. Experimental results

A typical experimental FID curve is reported in Fig. 1. This curve was taken in sample No. 1 with a preparative stage accomplished by a pulse of radiation inducing a Rabi frequency $\chi=0.34\times10^6$ rad/s and lasting a time $t_0=1.0$ ms. Both the initial steep rise and the decay part of the FID signal are visible in Fig. 1; however, as discussed above, the detection of the former part is probably unreliable. We are concerned here with the decay part. Figure 1 shows the extent to which this part of the experimental curve ($t \gtrsim 1.5$ μs) is well fitted by a single-exponential law with a rate $\Gamma/2\pi=(78\pm4)$ kHz over a large excursion (nearly 28 dB). This behavior is typical in the sense that in the whole investigated range of χ and in any sample we never found reliable evidence of multiexponential decay.

We have measured the dependence of Γ on the input power level. In these measurements care was taken in choosing the duration t_0 of the preparative stage. Too long pulses, especially at high power, cause undesired effects connected with liquid helium bubbling within the cavity, which breaks the tuning of the modes. On the other hand, a preparative stage lasting a time not long enough may leave the spin system far from its steady state. According to our experience, this circumstance may yield unreliable measurements of Γ. In fact, we have observed that an insufficient duration distorts the shape of the FID signal and especially its decay part, where small bumps appear; the consequence is an appreciable increase of the value of Γ obtained by the fitting procedure. In view of the relevance of this quantity for the considerations to be made later, we have retained only those measurements that could be taken with such a value of t_0 that halving it did not yield appreciable change in the FID signal. Moreover, only those measurements where a decay of at least 10 dB could be observed were considered as valid. These two requirements limited the investigated range of $\chi/2\pi$ from 3 to 200 kHz.

The results obtained in our three samples are reported in Figs. 2(a)–2(c), where Γ is plotted versus χ, both in frequency units. The experimental values of Γ were obtained by the fitting procedure outlined above and χ was measured by monitoring the TP-nutational regime[27] observable at the leading edge of the pump-radiation pulse. In each figure, we also report, for the sake of comparison, the theoretical behavior of Γ versus χ, as expected on the basis of BE (Eq. (9)] and in the Redfield high power [Eq. (10)]. As shown, on increasing χ, the experimental Γ values evolve from the Bloch limit toward the Redfield asymptote. The transition is completely observable in sample 1 [Fig. 2(a)], thanks to the particularly suitable value of T_1T_2. The measurements taken in sample No. 2 [Fig. 2(b)] attain the Redfield asymptote on the high-χ side, whereas data taken on sample 1 maintain an appreciable distance from this limit. The observed behavior in sample No. 3 [Fig. 2(c)] is intermediate.

In Table II we summarize the range of the main parameters (χ, χT_2, $\chi^2T_1T_2$, and Γ) explored in our experiments and in those reported in Refs. 6 and 8. Data reported in Table II suggests that the quantities $\chi^2T_1T_2$ and χT_2 control the range of χ in which the transition from the Bloch limit to the Redfield one occurs. In fact, relatively low values of T_1T_2 (as in Refs. 6 and 8, and in our sample No. 1) allow to detect in the low-χ side a behavior quite similar to that predicted by the BE. On the other hand, the Redfield theory seems to be valid at high values of χT_2, as in our sample No. 2. We note that the experimental data previously reported[6–8] maintain, even at high power, a large distance from the limit $\Gamma=\chi/\sqrt{2}$.

IV. COMPARISON WITH STOCHASTIC THEORIES

In several recent theories the non-Bloch properties of the FID signal are related to the time fluctuations of the frequency ω_{0i} of the individual centers. In these models, the stochastic nature of $\omega_{0i}(t)$ is responsible for the homogeneous linewidth (T_2^{-1}) but its effects are suppressed in the high-power regime $\chi\tau_c \gg 1$ where τ_c is the correlation time of $\omega_{0i}(t)$.[19] Several kinds of stochastic processes have been used to model $\omega_{0i}(t)$: The Ornstein-Uhlenbeck (OH) processes,[12,13,16] random-jump processes,[18] the Kubo-Anderson process,[15] and non-

Markovian processes.[14] None of the above theories succeeded to give full account of the experimental results reported up to now[6-8] and we confirm that the same is true for the results reported here. So, the aim of this section is not to single out the particular stochastic model or the approximation sequence that best fits our data. Rather, we will try to speculate about this failure and get suggestions for alternative models or interpretations. Our considerations are based on the comparison of our results with the theories employing the OU process for $\omega_{0i}(t)$, namely, a Gaussian process with an exponential correlation function. In agreement with our observations, this model yields a single-exponential FID signal for a wide range of χ, at least for $a\tau_c \ll 1$, where a is the standard deviation of the frequency density function.

Using this model Yamanoi and Eberly[13] obtained a simplified solution of the time evolution of the system during the FID regime. They got for the reversible decay rate $\gamma = \Gamma - 1/T_2$ (spectral width of the saturated packet line) an expression formally similar to that derived by the BE [Eq. (5)]

$$\gamma = (T_{2e})^{-1}(1+\chi^2 T_1 T_{2e})^{1/2} , \tag{11}$$

but with T_2 replaced by the effective T_{2e},

$$(T_{2e})^{-1} = (2T_1)^{-1} + a^2\tau_c/[1+(a\tau_c)^2] . \tag{12}$$

We recall that the expression of γ in Eq. (11) was obtained by neglecting the ϵ dependence of the relaxation matrix in the stochastic BE, which is equivalent to assume that the saturated lineshape of the individual packet keeps it original Lorentzian shape. By the way, we note that Eq. (12) is the same as previously derived[3,5] for describing the power dependence of T_2 in a dipolar-coupled or exchange-coupled spin system.

In Fig. 3 the experimental data obtained in our sample 1 are compared with the theoretical dependence calculated from Eqs. (11) and (12) using the experimental values of T_1 and of T_2. In this figure, data are reported as $\gamma/2\pi$ versus $\chi/2\pi$ in linear scales to conform to a widespread custom. If the condition $T_2^{-1} = a^2\tau_c$ is imposed, τ_c remains the only adjustable parameter. As shown in Fig. 3 it is not possible to find a value of τ_c that fits the experimental points, the discrepancy being well above the actual data scattering. However, as shown in the inset, the experimental points at low power (say, for $\chi/2\pi \lesssim 15$ kHz) seem to be well fitted by the theoretical curve drawn with $\tau_c = (50\pm5)$ μs. This value of τ_c implies $a\tau_c \simeq 0.8$, if a is derived from the experimental value of T_2, which saves the exponential shape of the FID signal.

The circumstance that Eqs. (11) and (12) give account of the experimental points only at low power suggests the possibility that the theory by Yamanoi and Eberly[13] is oversimplified in that it takes into account only one source of fluctuations. In fact, a possible interpretation of the fitting failure in Fig. 3 is that, on increasing χ, a fluctuation source with $\tau_c = 50$ μs is first made ineffective leaving room, for $\chi/2\pi \gtrsim 20$ kHz, to a different source with a shorter τ_c, which in turn will be suppressed at a higher value of χ. The effectiveness of more than one fluctuation source might give an account of the kinks ex-

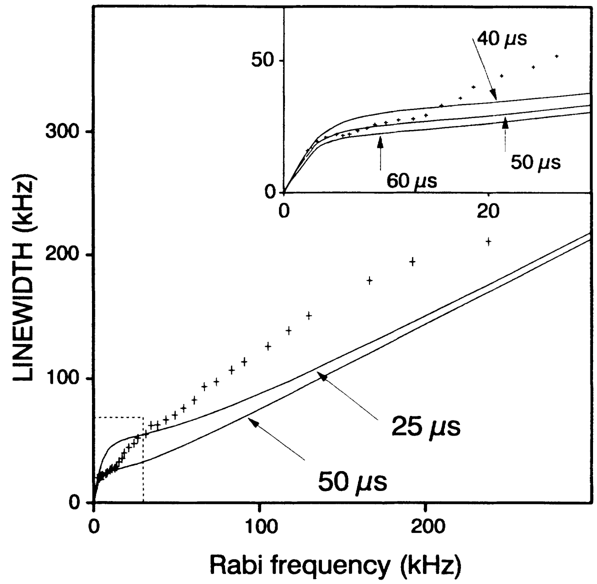

FIG. 3. The experimental values of the saturated linewidth $\gamma = \Gamma - 1/T_2$ obtained in sample 1 are compared with the model by Yamanoi and Eberly (Ref. 13). The theoretical curves are calculated from Eq. (11) for a few values of τ_c, as indicated in the figure. Both γ and χ are reported in frequency units. The low-power zone bounded by the dashed lines is expanded in the inset.

perimentally observed in the power dependence of γ. However we did not succeed in describing the experimental points by a mere sum of terms as in Eqs. (11) and (12) with different τ_c. A further indication comes from the fact that the experimental data taken in samples No. 2 and No. 3 [Figs. 2(b) and 2(c)] could not be fitted by Eqs. (11) and (12) in any power range. A reason for this may be that the validity condition of Eq. (11) involves either χT_2 or $\chi^2 T_1 T_2$, which are quite low in sample 1, rather than $\chi\tau_c$.

The departure of the experimental results from the predictions of Eq. (11) may be caused by the approximations used to solve the OU model in Ref. 13, namely, to neglect ϵ^α-dependent terms with $\alpha > 2$ in the stationary solution of the stochastic BE. These terms have been taken into account by Hanamura,[12] who succeeded in getting piecewise analytical expressions of the saturated linewidth γ in limited ranges of χ. In particular, in the intermediate power range $1 < \chi\tau_c < 4(T_1 T_2)^{1/2}$ he found

$$\gamma = (1/2\tau_c)[A + (A^2 - B^2)^{1/2}] \tag{13}$$

with $A = 1 + 3y^2/2$, $B^2 = y^4 + (1 - 4T_1/T_2)y^2 + 1$, and $y = \chi\tau_c$. The comparison of this theoretical power dependence with our experimental results on sample No. 1 is carried out in Fig. 4 for a few values of τ_c. As shown, the theoretical expression in Eq. (13) seems to fit the experimental points at intermediate values of χ, with a best fitting value of $\tau_c = (6.5\pm1.0)$ μs. This value of τ_c yields $a\tau_c = 0.3$, so that the condition $a\tau_c \ll 1$ is fulfilled. However, as shown in the inset of Fig. 4, the low-power experimental points once again seem to suggest the ex-

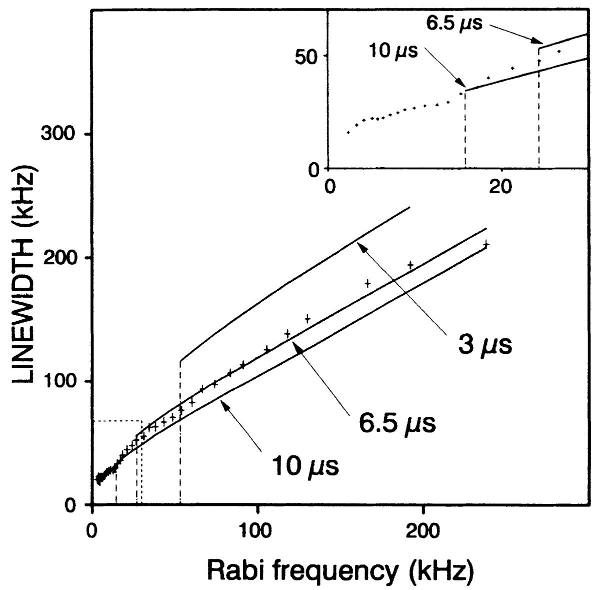

FIG. 4. The experimental values of the saturated linewidth $\gamma=\Gamma-1/T_2$ obtained in sample 1 are compared with the model by Hanamura (Ref. 12). The theoretical curves are calculated from Eq. (13) for a few values of τ_c, as indicated in the figure. Both γ and χ are reported in frequency units. For each value of τ_c, the curve is shown in its validity range. The low-power zone bounded by the dashed lines is expanded in the inset.

istence of more than one value of τ_c. Moreover, we note that the best fitting value of τ_c (6.5 μs) is consistent with the experimental value of T_2, but not with the measured decay times of the FID signal. In fact, we recall that to get the solution reported in Eq. (13) time averages over a time scale $t \gg \tau_c$ during the FID regime were used; on the contrary, the experimental FID signal decays in a time scale of a few microseconds. So, the agreement between experimental and theoretical results in the high-χ side of Fig. 4 is probably a coincidence rather than a proof of the adequacy of the model.

V. CONCLUSIONS

We have reported experimental data on the FID effect in a solid system containing two-level spin centers. In all the samples and in the whole investigated range of χ the FID signal is found to exhibit a single-exponential decay with a power-dependent rate. Our results confirm that the power dependence of the FID rate cannot be explained by an inhomogeneous-line model in which the generic spin packet obeys the conventional BE. In the high-power limit, our data are consistent with the existence of the Redfield asymptote $\Gamma=\chi/\sqrt{2}$, the approach to this limit being controlled by the condition $\chi T_2 \gg 1$, a condition which is not fulfilled in other experimental reports,[6–8] where a limited range of this parameter was examined. On the opposite low-power limit, in one of our samples it has been possible to confirm that the experimental values of γ agree with the power dependence predicted by the BE using the same value of T_2 as measured by spin-echo experiments. This fact, together with the exponential nature of both the FID and the echo signals, seems to answer in the affirmative the question whether at low intensities the Bloch theory is followed and capable of relating different effects.[16] We have shown that recent stochastic theories fail to give a satisfactory account for the observed power dependence. The effectiveness of more than one fluctuation source with different correlation times has been indicated as a possible origin of this failure. Other possibilities are connected with the inadequacy of the stochastic models considered up to now. Here we wish to mention that the difficulties met in explaining the power dependence of Γ may be related also to the oversimplified picture of the inhomogeneous line. In this regard we emphasize that the statement that the reversible decay part of the FID signal is the Fourier transform of the saturated homogeneous line shape, is somewhat misleading. In fact, the FID signal is in principle the convolution of the contributions coming from the whole distribution of spin packets and to relate it to the steady-state response of the generic packet is correct only if all the packets have the same line shape and width and are saturated only by the incoming radiation. The effectiveness of intraline spectral diffusion mechanisms, which may act on a given packet either as relaxation or saturation channel depending on its spectral position[20] or a distribution of the packet line widths may break the coincidence between the FID signal and stationary response of a particular packet. Further work is in progress in this direction.

To conclude, in our opinion, in spite of recent progresses, the coherence loss of strongly driven two-level systems in solids appears to be still an open problem which deserves further experimental and theoretical work.

ACKNOWLEDGMENTS

We gratefully acknowledge stimulating discussions with E. L. Hahn, A. E. Kaplan, and I. Oppenheim. We wish to thank E. Calderaro for taking care of sample irradiation in the γ-irradiator IGS-2 of Dipartimento Ingegneria Nucleare, Palermo, Italy. We thank G. Lapis and M. Quartararo for their continuous technical assistance. This work has been supported by Centro Interuniversitario Struttura della Materia and by Gruppo Nazionale di Struttura della Materia, Rome, Italy.

[1]A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon, Oxford, 1961); L. Allen and J. H. Eberly, *Optical Resonance and Two-Level Atoms* (Wiley, New York, 1985).

[2]A. G. Redfield, Phys. Rev. **98**, 1787 (1955).

[3]K. Tomita, Prog. Theor. Phys. **19**, 541 (1958).

[4]B. N. Provotorov, Zh. Eksp. Teor. Fiz. **14**, 1582 (1961) [Sov. Phys.—JETP **14**, 1582 (1961)]; V. A. Atsarkin and M. I. Rodak, Usp. Fiz. Nauk. **107**, 3 (1972) [Sov. Phys.—Usp. **15**, 251

(1972)].

[5]M. W. P. Strandberg, Phys. Rev. B **6**, 747 (1972); R. Boscaino, M. Brai, I. Ciccarello, and M. W. P. Strandberg, *ibid.* **7**, 50 (1973); R. Boscaino, M. Brai, and I. Ciccarello, *ibid.* **13**, 2798 (1976).

[6]R. G. DeVoe and R. G. Brewer, Phys. Rev. Lett. **50**, 1269 (1983).

[7]R. Boscaino, F. M. Gelardi, and G. Messina, Phys. Rev. A **28**, 495 (1983).

[8]A. Szabo and T. Muramoto, Phys. Rev. A **39**, 3992 (1989).

[9]T. Endo, T. Muramoto, and T. Hashi, Opt. Commun. **51**, 163 (1984); M. Yamanoi and J. H. Eberly, Phys. Rev. A **34**, 1609 (1986); A. Szabo and T. Muramoto, *ibid.* **37**, 4040 (1988).

[10]R. Boscaino, F. M. Gelardi, and R. N. Mantegna, Phys. Lett. A **124**, 373 (1987).

[11]A. G. Yodh, J. Golub, N. W. Carlson, and T. W. Mossberg, Phys. Rev. Lett. **53**, 659 (1984).

[12]E. Hanamura, J. Phys. Soc. Jpn. **52**, 2258 (1983); **52**, 3678 (1983); H. Tsunetsugu and E. Hanamura, *ibid.* **55**, 3636 (1986).

[13]M. Yamanoi and J. H. Eberly, Phys. Rev. Lett. **52**, 1353 (1984); J. Opt. Soc. Am. B **1**, 751 (1984).

[14]P. A. Apanasevich, S. A. Kilin, A. P. Nizovtsev, and N. S. Onishchenko, Opt. Commun. **52**, 279 (1984); J. Opt. Soc. Am. B **3**, 587 (1986).

[15]A. Schenzle, M. Mitsunaga, R. G. DeVoe, and R. G. Brewer, Phys. Rev. A **30**, 325 (1984); P. R. Berman and R. G. Brewer, *ibid.* **32**, 2784 (1985).

[16]J. Javanainen, Opt. Commun. **50**, 26 (1984).

[17]P. R. Berman, J. Opt. Soc. Am. B **3**, 564 and 572 (1986).

[18]K. Wodkiewicz and J. H. Eberly, Phys. Rev. A **32**, 992 (1985); A. R. Kessel, R. P. Shakhmuratov, and L. D. Eksin, Zh. Eksp. Teor. Fiz. **94**, 202 (1988) [Sov. Phys.—JETP **67**, 2071 (1988)].

[19]G. S. Agarwal and S. Singh, Phys. Rev. A **39**, 2239 (1989).

[20]T. G. Castner, Phys. Rev. **115**, 1506 (1959).

[21]P. F. Liao, J. E. Bjorkholm, and J. P. Gordon, Phys. Rev. Lett. **39**, 15 (1977); R. G. DeVoe and R. G. Brewer, Phys. Rev. A **20**, 2449 (1979).

[22]W. Gautschi, in *Handbook of Mathematical Functions,* edited by M. Abramovitz and A. Stegun (Dover, New York, 1970), p. 295.

[23]M. C. M. O'Brien, Proc. R. Soc. London Ser. A **231**, 404 (1955); A. L. Taylor and G. W. Farnell, Can. J. Phys. **42**, 595 (1964); R. H. D. Nuttal and J. A. Weil, *ibid.* **59**, 1696 (1981).

[24]R. A. Weeks and C. M. Nelson, J. Am. Ceram. Soc. **43**, 389 (1960); K. L. Yip and W. B. Fowler, Phys. Rev. B **11**, 2327 (1975); D. L. Griscom, *ibid.* **20**, 1823 (1979).

[25]R. Boscaino and F. M. Gelardi, Phys. Rev. A **35**, 3561 (1987).

[26]J. H. Shirley, Ph.D. thesis, California Institute of Technology, Pasadena, 1963 (unpublished); R. Boscaino, I. Ciccarello, C. Cusumano, and. M. W. P. Strandberg, Phys. Rev. B **3**, 2675 (1971); F. Persico and G. Vetri, *ibid.* **8**, 3512 (1973).

[27]R. Boscaino, F. M. Gelardi, and G. Messina, Phys. Rev. B **33**, 3076 (1986).

[28]R. Boscaino and G. Messina, Physica C **138**, 179 (1986).

[29]P. W. Milonni and J. H. Eberly, J. Chem. Phys. **68**, 1602 (1978).

[30]R. Boscaino, F. M. Gelardi, and R. N. Mantegna, in *Structure and Dynamics of Molecular Systems,* edited by R. Daudel *et al.* (Reidel, Dordrecht, 1985), p. 149.