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Satellite Free-Induction Signals in CdS:Mn

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Satellite free-induction signals occurring $\sim\frac{1}{4}\ \mu$sec after the main free-induction signal have been observed during pulsed microwave experiments with Mn^{2+} in CdS. These signals also appeared flanking the echo in an electron spin-echo experiment and were ~ 60 times weaker than the spin echo itself. When the Zeeman field was swept, the phase of the satellite signals underwent alternations, returning to any given value each time the field was changed by ~ 1.4 G. It is shown that these satellites originate in the superhyperfine interaction of Mn^{2+} with the nuclei Cd^{111} and Cd^{113}. The ease with which the satellites could be observed in spite of heavy broadening of the superhyperfine spectrum suggests that this may be a useful way of studying contact interactions in cases where the interaction is too weak to give a clearly resolved spectrum.

During recent electron spin-echo experiments performed with a sample of CdS doped with Mn, a group of unfamiliar satellite signals were observed in the vicinity of the applied pulses and the echo. These signals appeared $\sim\frac{1}{4}\ \mu$sec after the two applied pulses and $\sim\frac{1}{4}\ \mu$sec on either side of the spin echo (see Fig. 1). When allowance was made for phase-memory decay, it was found that all these satellites were more or less comparable in amplitude. The satellites on either side of the echo were,

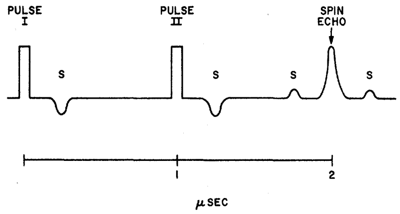

FIG. 1. Free-induction satellite signals (5) appearing in a two-pulse (120°–120°) electron spin-echo sequence for Mn^{2+} in CdS. The satellites appear $\frac{1}{4}$ μsec after pulses I and II and $\frac{1}{4}$ μsec on either side of the spin echo. The main free-induction signals following pulses I and II cannot be seen clearly, and their amplitudes cannot be determined because of microwave cavity ringing and instrumental overload effects. The ratio α between the amplitudes of the main induction signal and the satellite can, however, be inferred from the spin-echo signals.

however, ~ 60 times lower in amplitude than the spin echo itself. Signals of essentially the same kind were seen for all lines in the CdS : Mn spectrum and at all orientations of the Zeeman field.

The transmitted and received signals in the microwave apparatus were derived from and detected in synchronism with a single free-running klystron master oscillator. In a phase-coherent system of this kind, the spin echo can be displayed as a signal of either positive or negative sign. Once set, however, the sign of the signal remains the same as the Zeeman field is swept through the resonance.[1] If the echo is fed to a boxcar unit and thence to a pen recorder, the apparatus can be made to give the EPR spectrum of the material as illustrated in Fig. 2(a). A trace markedly different from the usual type of boxcar tracing was obtained when the boxcar gate was set to cover a satellite signal instead of the spin echo [see Fig. 2(b)]. The envelope of the trace still corresponded roughly to the CdS : Mn spectrum but the signal itself oscillated between positive and negative values with a period ~ 1.4 G. Similar tracings, with an oscillation of approximately the same period, were obtained at other settings of the Zeeman field.

The appearance of a satellite after a single microwave pulse (pulse I) suggested that the satellite might be a form of free-induction signal. In this case, its subsequent appearances on either side of the spin echo would merely illustrate the general rule that a spin-echo signal consists of two free-induction signals back to back. Results of previous studies[2,3] of spin resonance in CdS : Mn allow one to confirm this hypothesis as we now show.

The Mn^{2+} ion substitutes for Cd^{2+} in the CdS lattice. There are 12 near-neighbor Cd atoms at approximately the same distance from the Mn^{2+} ion and two Cd isotopes Cd^{111} and Cd^{113}. These isotopes have relative abundances 12.86 and 12.34%, spin $I=\frac{1}{2}$, and similar nuclear moments. The interaction between an Mn^{2+} spin and a Cd nuclear moment at any of these sites can be adequately described by a single type of contact term $A_{Cd}\vec{I}\cdot\vec{S}$ where $A_{Cd}/\hbar = 7.8$ MHz. Since any given site may be occupied by a Cd atom with nuclear spin up or down, or occupied by a Cd atom with no nuclear moment at all, the effect of this contact interaction is to split the Mn^{2+} electron resonance into a total of 25 components each separated from the next by $0.5A_{Cd}/\hbar$. The intensity distribution of these superhyperfine components is given in Refs. 2 and 3.

Before going on to analyze this somewhat complex situation, let us first consider the simpler case of an electron spin surrounded by n equivalent sites at each of which there is a single standard type of nuclear moment with $I=\frac{1}{2}$ and $M_I=\pm\frac{1}{2}$. The intensity distribution is then given by the coefficients of the binomial series $(a+x)^n$. For even n,[4] the superhyperfine spectrum before line broadening is taken into account can be described by the series

$$S_n^{(0)}(\omega)=(0.5)^n\{{}_nC_{0.5n}\delta(\omega)+{}_nC_{0.5n-1}[\delta(\omega_s-\omega)+\delta(\omega_s+\omega)] + \cdots + [\delta(0.5n\omega_s-\omega)+\delta(0.5n\omega_s+\omega)]\}. \quad (1)$$

The terms are symmetrically arranged about $\omega=0$, the full microwave resonance frequency being $\omega_0+\omega$, where ω_0 is the Larmor frequency in the absence of superhyperfine interactions. Each of the components in (1) are broadened as a result of magnetic dipolar interactions with other Mn^{2+} ions in the sample. It can be shown by means of the sta-

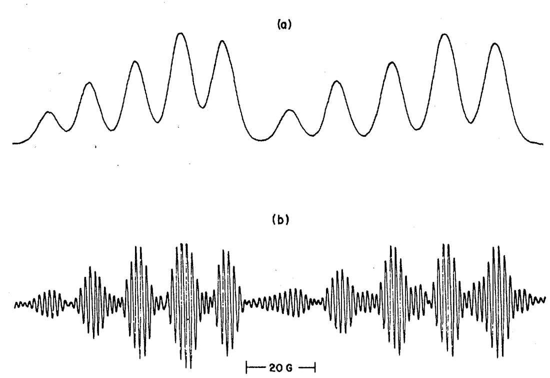

FIG. 2. (a) Boxcar tracing of a portion of the CdS : Mn spectrum with the boxcar gate set on the electron spin-echo signal. The angle between the CdS c axis and the Zeeman field is 28°. The microwave field intensity H_1 was 0.5 G. (b) Boxcar tracing of the same portion of the CdS : Mn spectrum with the boxcar gate set on the satellite S following a single microwave pulse. The period of the oscillation is ~ 1.4 G. The microwave field intensity H_1 was 1.5 G. Values of H_1 ~ 6 G (as used in other experiments) yield a similar trace, but the resemblance to the normal EPR spectrum (a) is partially obscured on account of the excitation of more than one EPR line at a time.

tistical theory of line broadening that this interaction broadens each monochromatic spin packet into a Lorentzian

$$S_L(\omega)=\omega_L/\pi(\omega^2+\omega_L^2)\ . \tag{2}$$

Thus, we have a spectrum $S_n(\omega+\omega_0)$ where the line-shape function is

$$S_n(\omega)=\int S_L(\omega-\omega')S_n^{(0)}(\omega)\,d\omega'\ . \tag{3}$$

Under ideal conditions of the microwave pulsing experiment[5] (i.e., with the microwave field H_1 large enough so that γH_1 is greater than the width of the spectrum), the free-induction signal $I_n(t)$ is proportional to the Fourier transform ($\mathfrak{F}$) of $S_n(\omega+\omega_0)$. Shifting the origin and applying the convolution theorem, we find that $\mathfrak{F}(S_n(\omega+\omega_0))=e^{i\omega_0 t}\mathfrak{F}(S_L(\omega))\times\mathfrak{F}(S_n^{(0)}(\omega))$. The Fourier transform of $S_L(\omega)$ is $e^{-\omega_L|t|}$. The Fourier transform of $S_n^{(0)}(\omega)$ is the series

$$0.5^n[{}_nC_{0.5n}+{}_nC_{0.5n-1}(e^{i\omega_s t}+e^{-i\omega_s t})+\cdots]\ ,$$

which is the binomial expansion of

$$0.5^n(e^{i\omega_s t/2}+e^{-i\omega_s t/2})^n=[\cos(1/2\omega_s t)]^n\ .$$

We thus have

$$I_n(t)=e^{i\omega_0 t}(\cos\tfrac{1}{2}\omega_s t)^n e^{-\omega_L|t|}\ . \tag{4}$$

In the more general case where there are N equivalent sites, some not occupied by magnetic nuclei, the probability of finding a configuration with n out of N magnetic neighbors is given by $P_N^n=p^n(1-p)\times(1-p)^{N-n}\,{}_NC_n$, where p is the fraction of nuclei having a magnetic moment. The induction signal due to all such configurations then becomes

$$I_N(t)=\sum_{n=0}^{N}P_N^n I_n(t)\ .$$

Hence,

$$I_N(t)=e^{i\omega_0 t}e^{-\omega_L|t|}\sum_{n=0}^{N}p^n(1-p)^{N-n}\,{}_NC_n(\cos\tfrac{1}{2}\omega_s t)^n\ . \tag{5}$$

Equation (5) can be simplified by replacing the binomial series with its sum and by performing a minor trigonometrical manipulation, giving

$$I_N(t)=e^{i\omega_0 t}e^{-\omega_L|t|}(1-2p\sin^2\tfrac{1}{4}\omega_s t)^N\ . \tag{6}$$

If we take the Cd^{111} and Cd^{113} nuclei as a single species, then $p\sim 0.25$. The term $1-2p\sin^2\frac{1}{4}\omega_s t$ is in this case always positive, and has maxima at $t=0$, $4\pi/\omega_s$, $8\pi/\omega_s$, etc. Substituting $\omega_s/2\pi=7.8$ MHz, we find that these times are approximately 0, $\frac{1}{4}$, $\frac{1}{2}$ μsec, etc. The first maximum corresponds to what we have called earlier the "main" free-induction signal. The maximum at $t=t_1=4\pi/\omega_s$ is the observed satellite and is attenuated by a factor

$$\alpha=e^{4\pi\omega_L/\omega_s}\ . \tag{7}$$

Subsequent satellites would be attenuated by factors of α^2, α^3, etc. The phase of the first satellite is determined by the factor $e^{i\omega_0 t}=e^{i\omega_0 t_1}=e^{4\pi i\omega_0/\omega_s}$. As the Zeeman field H_0 is swept, ω_0 changes, and the argument $4\pi\omega_0/\omega_s$ increases by 360° for each increment $\Delta H_0=\omega_s/2\gamma$. Hence the pattern of signal reversals [Fig. 2(b)] obtained when this satellite is detected in a phase-coherent system. The ratio α cannot be found from the free-induction signals emitted immediately after a microwave pulse because the main signal is obscured by cavity ringing and by instrumental overload effects. It will, however, be the same as the ratio between the main peak and the satellites in the spin echo. Since $\alpha\sim 60$ in our sample, only one of the satellites predicted by Eq. (4) could be seen.

The form of the main signal and of the satellites can be approximated by a Gaussian function. Writing $\exp\{-[0.5N(\omega_s t/4)^2]\}$ for $[1-0.5\sin^2(\omega_s t/4)]^N$ we find the half-width of the first peak (and also of subsequent peaks) in $I_N(t)$ between e fall points is approximately given by

$$(\Delta t)_{1/2}=(4/\omega_s)(0.5N)^{-1/2}\ . \tag{8}$$

Substituting $\omega_s/2\pi=7.8$ MHz, $N=12$, we obtain $(\Delta t)_{1/2}\simeq 33$ nsec. This width is well in excess of the time difference $t_1(Cd^{111})-t_1(Cd^{113})\simeq 11$ nsec between the first satellite peaks corresponding to each of the groups of magnetic nuclei considered separately, and justifies us in treating Cd^{111} and Cd^{113} as a single group. We can also use the Gaussian approximation to derive a simple form for the frequency spectrum in the region of its maximum intensity. Let us assume that the satellite attenuation factor α is large so that the free-induction signal can be adequately represented by the main signal and first satellite. We then have

$$\exp[-t^2/(\Delta t)_{1/2}^2]+(1/\alpha)\{\exp[-(t-t_1)^2/(\Delta t)_{1/2}^2]+\exp[-(t+t_1)^2/(\Delta t)_{1/2}^2]\}\ ,$$

where the time function has been symmetrized about $t=0$. Transforming into the frequency domain we obtain

$$S(\omega)-\omega_0\propto\{\exp[-(\Delta t)_{1/2}^2\omega^2/2]\}[1+(2/\alpha)\cos\omega t_1]\ . \tag{9}$$

The broadened superhyperfine spectrum is thus approximately given by a Gaussian function of half-width $\sqrt{2}/(\Delta t)_{1/2}$ between e fall points modulated to a depth $(1/\alpha)$ by a cosine term of period $t_1=4\pi/\omega_s$. In our case, this corresponds to a half-width $\simeq 6.8$ MHz, a period of 0.25 μsec, and a "modulation depth" $1/\alpha\sim 2\%$, the last being derived from the experimental value of the satellite attenuation factor. Not surprisingly, we were unable to see the superhyperfine structure directly in the EPR spectrum.

Calculations indicate that the broadening was anomalously large. The nominal concentration of Mn^{2+} ions was 0.01%. Applying the statistical theory of broadening to the case of Mn^{2+} in the high-temperature limit, we obtain the dipolar width

$$\omega_D = 7.6\hbar\,\gamma^2 n_{\mathrm{Mn}}\ ,$$

which, for $n_{\mathrm{Mn}} = 1.78\times 10^{18}$ ions/cm^3, yields $\omega_D/2\pi \sim 0.7$ MHz ($\sim\frac{1}{4}$ G). However, the width $\omega_L/2\pi$ inferred by substituting $\alpha = 60$ and $\omega_s/2\pi = 3.9$ MHz in Eq. (7) is 2.7 MHz. This could mean that the actual concentration of Mn^{2+} was several times greater than the nominal value, or that the broadening was increased by clustering of Mn^{2+} ions. It does not seem likely that broadening was due to strains since the attenuation factor α was essentially the same in the $M_s = +\frac{1}{2} \rightleftarrows -\frac{1}{2}$ transitions in the others.

Some care must be taken when applying these results to systems other than CdS : Mn. For example, if all the nuclei are identical and have magnetic moments (i.e., $p = 1$), then, by Eq. (4), the modulus $|I_N(t)| \equiv |I_n(t)|$ has maxima at $t = 0$, $2\pi/\omega_s$, $4\pi/\omega_s$, etc. These maxima are twice as closely spaced as in the case considered earlier, and the attenuation factors must be modified accordingly. As p is reduced from 1 to 0.5, the maxima at $2\pi/\omega_s$, $6\pi/\omega_s, \ldots$ become weaker leaving only the set at 0, $4\pi/\omega_s, \ldots$ for values of $p \leq 0.5$. In the range $1 \leq p \leq 0.5$ the peak amplitudes for the two sets are $e^{-\omega_L|t|}$ and $(1-2p)^N e^{-\omega_L|t|}$, the second set being reversed in sign with respect to the first set if N is odd.

Since the occurrence of superhyperfine interactions is not unduly rare, one may ask why induction-signal satellites have not been seen in other materials. The superhyperfine spectra due to interactions with F^{19} nuclei can, for example, be clearly resolved in the EPR spectra of some paramagnetic ions substituted[6] in CaF_2. Moreover, as we have shown here, a satellite induction signal may be easy to see even when the superhyperfine structure is obscured by broadening effects. One difficulty in the way of observing superhyperfine structures arising from F^{19} or from H^1 by means of free-induction methods lies in the magnitude of the interaction $\hbar\omega_s$. Large values of H_1 and correspondingly short 90° pulses are therefore needed to span the spectrum. If H_1 is insufficient, the superhyperfine components lying $>\gamma H_1$ away from the microwave resonance frequency will not contribute significantly to the free-induction signal, and it will be as if the number n had been reduced, thus widening the satellite signal and causing it to merge with the main induction signal. This difficulty would probably not be a serious one in some cases of interest. Short pulses ~ 10 nsec in duration, and fields H_1 such that $\gamma H_1/2\pi \sim 25$ MHz can readily be obtained by current techniques. These should suffice for observations of satellite induction signals due to superhyperfine interactions with such nuclei as N^{14} or H^2.

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[1]It is assumed here that $\gamma H_1 < \Delta\omega_L$, where γ is the gyromagnetic ratio $g\beta/\hbar$, H_1 is the microwave magnetic field, and $\Delta\omega_L$ is the half-width of the resonance line.

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[4]For odd n, Eq. (1) has a slightly different form. The argument follows the same lines, however, and leads to exactly the same expression for $I_n(t)$ [Eq. (4)].

[5]This condition is not essential but serves to simplify the argument here. The effect of having $\gamma H_1 \lessapprox$ width of spectrum is discussed briefly at the end.

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