Coherence Effects in Inhomogeneously Broadened EPR Lines of Nitrogen in Silicon Carbide

I. B. Baumberg, D. M. Daraseliya, and T. I. Sanadze

Tbilisi State University

Submitted September 13, 1971

Zh. Eksp. Teor. Fiz. **62**, 1049–1053 (March, 1972)

A periodic trough structure has been found to appear in inhomogeneously broadened EPR lines of nitrogen in silicon carbide after irradiation with microwave pulses with a duration shorter than the spin-spin relaxation time T_2. The patterns observed are explained as the result of rotation of the magnetization vectors of the spin packets by the coherent microwave pulses. By taking into account the nonuniformity of the distribution of the amplitude H_1 of the high-frequency magnetic field, theoretical patterns for the periodic trough structures are constructed and are in good agreement with experiment.

THE study of the dynamics of EPR lines, and of inhomogeneously broadened lines in particular, is of considerable interest in the physics of magnetic resonance. We have investigated the effect of short microwave pulses on the EPR spectrum of nitrogen in silicon carbide and have detected coherence effects that have not been observed previously.

The experiments were carried out on a superheterodyne radio-spectrometer in the 3-cm range of wavelengths at liquid-helium temperatures. The technique applied was analogous to that used for the observation of discrete saturation of EPR lines[1,2], the saturation of the spectrum being carried out by means of a separate klystron. The concentration of impurity nitrogen in the silicon carbide (6H SiC) samples amounted to 5×10^{17} and 8×10^{17} cm^{-3}.

The EPR spectra of nitrogen in this substance have been sufficiently well studied[3-5], and the spin-lattice relaxation was investigated in the papers[6,7]. The inhomogeneous broadening of the components of the EPR spectrum is due to the super-hyperfine interaction of nitrogen donor electrons with the magnetic nuclei Si^{29} and C^{13}. The width of the spectral components in the sample with a nitrogen concentration of 5×10^{17} cm^{-3}, which we studied in the most detail, was 2 Oe.

On saturation of the nitrogen EPR line by powerful microwave pulses of duration $\tau \sim 10^{-4}$—10^{-5} sec, in addition to the central hole "burned out" directly, two symmetrically placed satellite troughs, at a distance from the central trough equal to the nuclear Zeeman frequency of Si^{29}, were observed to appear. The appearance of these troughs was studied earlier[6], and can be explained by the saturation of "forbidden" transitions of donor electrons.

The action of microwave pulses of duration less than 10^{-5} sec on any of the components of the spectrum leads to the appearance of a periodic trough structure (PTS), symmetric about the point of saturation, in the line (Fig. 1a); the "frequency" of these troughs increases smoothly with increase of the microwave pulse duration[1)]. On displacement of the point of application of the microwave pulse along the contour of the EPR line, the whole PTS pattern is shifted correspondingly, the "frequency" of the troughs remaining unchanged. With decrease of the pulse duration to $\tau = 4 \times 10^{-7}$ sec, the PTS degenerates into a single hole.

It was found that the extent of the PTS and the depth of the troughs grow with increase of the power of the microwave pulses; however, their "frequency" remains unchanged, within the limits of experimental error. For a given power and duration of the microwave pulses, the PTS pattern is fixed on the line and, together with the line, proportionally contracts or expands with change of the depth of modulation of the magnetic field.

The characteristic time for the "filling in" of the observed PTS as a result of cross-relaxation processes is approximately equal to 30 msec, as can be seen from Fig. 1b. (For the central component of the spectrum, the spin-lattice relaxation time of the donor

[1)]The occasionally observed asymmetry of the PTS about the point of saturation is evidently due to non-monochromaticity of the microwave pulses.

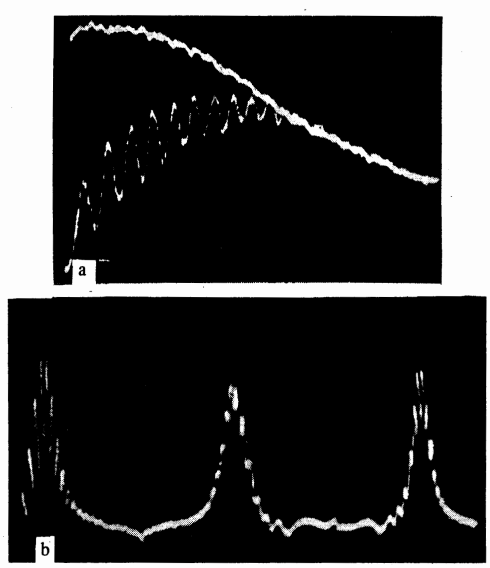

FIG. 1. a) Oscillogram of a portion of the equilibrium EPR lineshape of nitrogen in SiC (upper) and the PTS pattern (lower) arising in it after the action of a microwave pulse. b) Oscillogram illustrating the "filling in" of the PTS in the course of a few cycles of the magnetic modulation (50 Hz, nitrogen concentration 5×10^{17} cm^{-3}).

electrons in this sample is equal to $T_1 \approx 1.5$ sec at $T = 1.7°K$, and the cross-relaxation time $T_{21} \approx 50$ msec.)

The presence of a PTS in the EPR line was also verified in the absence of magnetic-field modulation. For this, we investigated the curves of the recovery of the central packet of the line after irradiation by a microwave pulse at the neighboring packets, as a function of the magnitude of the detuning between them. It was found that, with change of the detuning, the amplitudes of the relaxation curves vary in magnitude in accordance with the PTS pattern observed in the presence of magnetic field modulation and with the same microwave pulse duration.

Inasmuch as estimates of the spin-spin relaxation time of the packets give $T_2 \sim 10^{-5}$ sec,[2)] and the duration of the microwave pulses in our experiments was $\tau < 10^{-5}$ sec, the appearance of the PTS can be explained by the presence of coherence effects in the inhomogeneously broadened EPR line.

A coherent microwave pulse induces rotations of the magnetization vectors of the separate spin packets through angles determined by the values of the corresponding effective magnetic fields and by the pulse duration τ. In a time lapse of order T_2 after the action of the pulse, the transverse components of the magnetization vectors disappear, and the corresponding longitudinal components $M_Z(\omega)$ determine the resulting EPR line-shape. The dynamics of the line are then determined by the cross-relaxation processes and spin-lattice relaxation.

The angle θ through which the magnetization vector **M** in the rotating coordinate frame is rotated as a result of the action of a microwave pulse of duration τ is determined by the expression $\theta = (\omega_1^2 + \delta^2)^{1/2}\tau$, where $\omega_1 = \gamma H_1$, H_1 is the amplitude of the microwave magnetic field, and $\delta = \omega - \omega_0$ is the detuning between the frequency ω_0 of the microwave pulse and the frequency ω of the free Larmor precession.

We consider now an inhomogeneously broadened line and assume that the spin packets are distributed continuously and that a microwave pulse of frequency ω_0 is applied to the center of the line, its amplitude H_1 being much smaller than the width Δ of the inhomogeneous line, $H_1 \ll \Delta$. Under these conditions, the resulting EPR line-shape is determined by the expression[8,9] 3)

$$\frac{M_{z,\tau}}{M_0} = g(\delta)\left\{1 - \frac{\omega_1^2}{\omega_1^2+\delta^2}\left[1-\cos(\omega_1^2+\delta^2)^{1/2}\tau\right]\right\}, \qquad (1)$$

where M_0 is the equilibrium magnetization, $M_{Z,\tau}(\omega)$ is a magnetization component of the spin packet with frequency $\omega = \delta + \omega_0$, and $g(\delta)$ is the shape function of the inhomogeneously broadened line.

Formula (1) gives a qualitatively correct description of the experimentally observed PTS. For $\omega_1\tau = \pi/2$ (at exact resonance $\delta = 0$), this structure degenerates into a single hole, and this enables us to determine the effective value of the amplitude H_1. In Fig. 2a is given the shape of the single hole after the action of a 90-degree pulse of duration $\tau = 4 \times 10^{-7}$ sec at the point $\delta = 0$, from which the effective value was found to be $H_1 = 0.2$ Oe under the conditions of our experiment. We can now construct theoretical PTS curves with the same value of H_1 and for different pulse durations τ. In doing this, it is necessary to take into account the distribution of the amplitude H_1 in the volume of the sample. That this is necessary is indicated by the fact that, for any pulse durations τ, the observed PTS pattern has a minimum at the saturation point $\delta = 0$, whereas, according to formula (1), this point should oscillate as a function of the pulse duration τ. Superposition of the periodic structures from different parts of the sample leads to averaging of the observed pattern in the region of values $\delta < \omega_1$. Taking into account the distribution of the electromagnetic field in the volume of a sample having dimensions $8 \times 8 \times 2$ mm, and the distortions introduced into this distribution by the dielectric properties of the material investigated, we can give a rough estimate of the extent of scatter of the amplitude H_1 within the volume of the sample and, for simplicity, assume a smooth distribution.

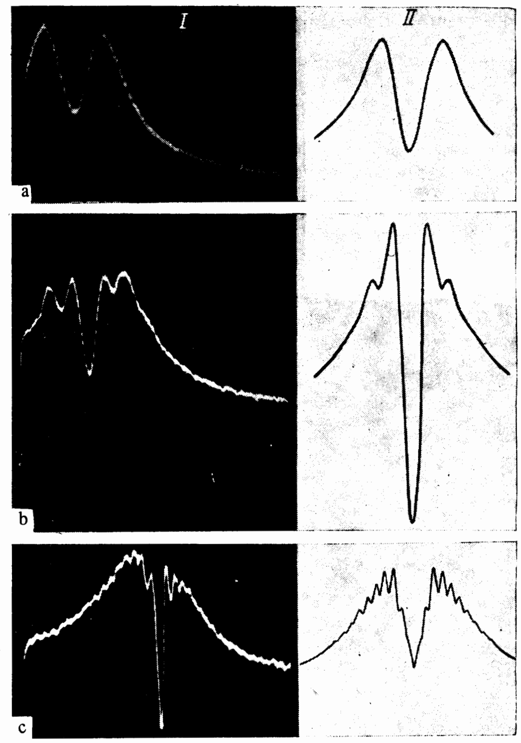

FIG. 2. Oscillograms of the PTS (left) and calculated PTS shapes (right) for the following microwave pulse durations: a) $\tau = 4 \times 10^{-7}$ sec, b) $\tau = 8 \times 10^{-7}$ sec, c) $\tau = 2.5 \times 10^{-6}$ sec.

In Fig. 2 on the left, oscillograms are given of the PTS at constant power and different microwave pulse durations. The corresponding theoretical curves are shown on the right in Fig. 2. They were calculated from the formula

$$\frac{M_{z,\tau}(\delta)}{M_0} = \frac{g(\delta)}{\omega_1''-\omega_1'}\int_{\omega_1'}^{\omega_1''}\left\{1 - \frac{\omega_1^2}{\omega_1^2+\delta^2}\left[1-\cos(\omega_1^2+\delta^2)^{1/2}\tau\right]\right\}d\omega_1, \qquad (2)$$

2)The time T_2 can be estimated from the minimum width of the hole burned out by a purely saturating pulse.

3)Mims et al.[9], who treated theoretically the effect of a coherent microwave pulse on an inhomogeneously broadened line, did not detect experimentally the expected pattern of troughs in the EPR lines of Ce^{3+}, Er^{3+}:$CaWO_4$; they ascribed this to substantial nonuniformity of the distribution of the amplitude H_1 in the volume of the sample.

where $\omega_1' = \gamma H_1'$, $\omega_1'' = \gamma H_1'$, $\gamma = g\beta/\hbar$, $g = 2$, $H_1' = 0.1$ Oe, and $H_1'' = 0.3$ Oe; the function $g(\delta)$ was taken to be a Lorentzian with width 2 Oe.

If we allow for the crudeness of the approximations and estimates used, the agreement between the constructed and the experimental curves is completely satisfactory. The agreement with experiment of the positions of the troughs in the calculated periodic structures is better than the agreement of their intensities and of the widths of the central troughs with experiment. Since ω_1 is much smaller than the width of the inhomogeneous line, the positions of the troughs in the region of detunings $\delta > \omega_1$ is almost independent of the distribution of the amplitude H_1 in the volume of the sample, whereas in the region of the central trough $\delta < \omega_1$, the calculated curves depend essentially on the estimate of the amplitude H_1 and on the choice of its distribution function.

From the disappearance of the PTS with increase of the microwave pulse duration, we can estimate the spin-spin relaxation time T_2; in the given sample, it was found to be equal to $T_2 \sim 10^{-5}$ sec. A more accurate estimate of this time can be made, apparently, from the maximum PTS "frequency" at which this structure can still be resolved.

The authors thank G. R. Khutsishvili, L. L. Buishvili and M. D. Zviadadze for useful discussion, and O. G. Khakhanashvili and M. S. Tsarakhov for assistance in the work.

[1]P. I. Bekauri, B. G. Berulava, T. I. Sanadze, and O. G. Khakhanashvili, Zh. Eksp. Teor. Fiz. **52**, 447 (1967) [Sov. Phys.-JETP **25**, 292 (1967)].

[2]A. A. Manenkov and V. A. Milyaev, Zh. Eksp. Teor. Fiz. **58**, 796 (1970) [Sov. Phys.-JETP **31**, 427 (1970)].

[3]J. S. van Wieringen, p. 367 of Semiconductors and Phosphors, (ed. M. Schön and H. Welker), Interscience, N.Y., 1958.

[4]H. H. Woodbury and G. W. Ludwig, Phys. Rev. **124**, 1083 (1961).

[5]I. M. Zaritskiĭ, L. A. Shul'man, and I. N. Geĭfman, Fiz. Tverd. Tela **11**, 30 (1969) [Sov. Phys.-Solid State **11**, 22 (1969)].

[6]I. B. Baumberg, T. I. Sanadze, O. G. Khakhanashvili, and M. S. Tsarakhov, Soobshch. Akad. Nauk Gruz. SSR (Reports of the Academy of Sciences of the Georgian SSR) **60**, 313 (1970).

[7]I. M. Zaritskiĭ, A. A. Konchits, and L. A. Shul'man, Fiz. Tverd. Tela **13**, 1895 (1971) [Sov. Phys.-Solid State **13**, 1588 (1972)].

[8]A. Abragam, The Principles of Nuclear Magnetism, Oxford, (1961) [Russ. transl., Ill, M., p. 25, 1963].

[9]W. B. Mims, K. Nassau, and J. D. McGee, Phys. Rev. **123**, 2059 (1961).

Translated by P. J. Shepherd
126