that this technique may be generally applicable to many of the important deep-level defects in silicon.

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[a]Permanent address: Physikalisches Institut (Teil 4) der Universität Stuttgart, Pfaffenwaldring 57, D-7000 Stuttgart 80, Federal Republic of Germany.

[b]Permanent address: Department of Physics, The University, Hull, England.

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Observation of Electron Paramagnetic Resonances at Multiples of the "Classical" Resonance Magnetic Field

B. Clerjaud and A. Gelineau

Laboratoire de Luminescence II, Université Pierre et Marie Curie, F-75230 Paris 05, France

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Observation of electron paramagnetic resonance signals at multiples (up to 7) of the conventional magnetic resonance field are reported in the case of the system GaP:Cr^+ at low temperatures. These signals are shown to be due to multiphoton transitions. The physical reason for the observation of these resonances is a long relaxation time consistent with the physical nature of this paramagnetic center.

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Resonant multiphoton absorption in magnetic resonances has been known to exist since the optical pumping experiments of Margerie and Brossel,[1] which have been interpreted by Winter.[2,3] In these experiments the amplitude $2H_1$ of the microwave magnetic field and the static magnetic field H were of the same order of magnitude. To our knowledge such resonances have never been reported in nuclear magnetic resonance nor in electron paramagnetic resonance (EPR). In this Letter, we report the observation of such multiphoton resonances in EPR experiments in which H_1/H is as low as 10^{-5}. We will show that these resonances can be observed because of the long re-

laxation time of the studied paramagnetic system, GaP:Cr^+.

EPR of isolated Cr^+, presumably on a gallium site, is well known in gallium phosphide.[4] It consists of a single line characterized by $g = 1.999$ and a linewidth of 130 G.[4] Performing experiments on GaP:Cr samples we observed, in addition to the well known "classical" Cr^+ line, other lines situated at multiples (up to 7) of the magnetic field of the "classical" line. Figure 1 shows the EPR spectrum induced by red light in a semi-insulating GaP:Cr sample (Siemens V 772 E). This spectrum has been obtained at 3.5 K, the microwave (9.2 GHz) power incident on the cavity being 20 dB below the power of the conventional Varian X-band EPR klystron, i.e., of the order of 5 mW in a cavity whose quality factor is smaller than 1000. In this spectrum, one clearly sees three lines: The main line situated at H_0 is the "classical" Cr^+ line; the two others are situated at $2H_0$ and $3H_0$. At higher microwave power, one observes other lines at (4, 5, 6, and 7)H_0. The Cr^+ concentration of that sample under illumination is only 10^{15} cm^{-3}.[5]

The lines at nH_0 $(n>1)$ are undoubtedly associated with the same center as the line at H_0 (i.e., Cr^+) for the following reasons: (i) They have the same behavior with the exciting light wavelength as the "classical" line, (ii) they have the same behavior with the exciting light intensity as the "classical" line, (iii) they have the same linewidth (130 G) as the "classical" line; this inhomogeneous linewidth is due to the interaction of the Cr^+ electrons with the ligands' nuclear spins and is characteristic of the Cr^+ center. It is to be noted that all these lines are observed in the dark n-types samples.

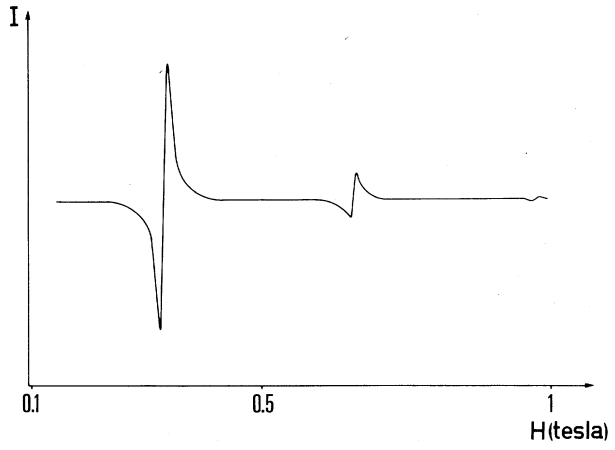

FIG. 1. Light-induced EPR spectrum of a GaP:Cr semi-insulating sample; $T = 3.5$ K.

A priori, there are two ways to explain these extra transitions: (i) multiphoton transitions, (ii) absorption of harmonics of the microwave frequency generated by the sample. We performed two experiments the results of which rule out the second hypothesis. In the first one, we placed in the cavity in addition to a GaP:Cr sample another sample ($ZnS:Mn^{2+}$) having a very strong EPR signal; we could only observe lines at nH_0 $(n>1)$ of the GaP:Cr^+ signal. In the second one, we looked at GaP samples having in addition to the GaP:Cr^+ other very strong signals (donor resonances or Fe^+); again it has only been possible to detect lines at nH_0 $(n>1)$ for the Cr^+ center. These experiments exclude the effect of harmonics of the microwave and prove that we are dealing with multiphoton transitions.

The conservation of energy is obviously satisfied for these transitions, the energy splitting between two consecutive levels being $n\gamma H_0 = n\hbar\omega$. The conservation of angular momentum is less obvious especially for n even and one has to look in detail at the experimental setup in order to understand it. The microwave cavity that we use is a rectangular TE_{102} cavity. In the empty cavity, the microwave magnetic field $\vec{H}_1$ at the center of the cavity is linearly polarized and is perpendicular to the static magnetic field $\vec{H}$. In this cavity we insert a cryostat consisting of three coaxial quartz tubes whose dielectric constant is of the order of 4 and of course we insert in the cryostat the GaP sample whose dielectric constant is of the order of 11. As a consequence, the cryostat and the sample bend the microwave field lines and allow a component H_{1z} of $\vec{H}_1$ along the static magnetic field. This bending of the microwave field lines in our experimental setup has been proved by the observation of cyclotron resonance signals.[6] Unfortunately, the component H_{1z} induced by this experimental configuration is very inhomogeneous. The H_1 component perpendicular to $\vec{H}$ consists of circularly polarized σ_+ and σ_- photons which carry, respectively, the angular momenta $+\hbar$ and $-\hbar$. The H_{1z} component consists of π photons carrying no angular momentum. The existence of these π photons in our experimental setup explains the observation of the even resonances.

In order to analyze the physical mechanism which allows the observation of these extra resonances, we have looked at the variation of the spectra when one increases the temperature. The

intensity of these $n>1$ resonances decreases rapidly when the temperature is increased. At about 10 K they are no longer observable; it is to be noted that the "classical" $n=1$ signal is still well observed at this temperature: It can even be observed at liquid-nitrogen temperature. This experiment suggests that a parameter varying strongly with temperature is at the origin of the observation of these $n>1$ lines, and one is led to think of the relaxation time of the paramagnetic center.

We have solved the Bloch equations in order to get more precise information about the origin of the observation of these extra resonances. In the general case corresponding to our experiment, i.e., with one component of $\vec{H}_1$ parallel to $\vec{H}$ and another one perpendicular to it, the Bloch equations are quite complex to solve and computation is necessary; the details of these calculations will be published elsewhere. The main result is that the $n>1$ resonances are solutions of the Bloch equations; the absorbed power varies as $|\vec{H}_1|^{2n}$ at low power in accordance with Winter's calculations,[3] i.e., as the nth power of the number of photons. In our experiment we use a reflection cavity and a linear detector, i.e., we do not detect the absorbed power, but the magnetization which is varying as $|\vec{H}_1|^{2n-1}$ at low power. In Fig. 2 we have plotted the intensity of the EPR signal versus the microwave power. We have not been able to work at sufficiently low power in order to be in the linear part of the saturation curves, but it is clear that the low-power slopes of these curves increase strongly with n. In Fig. 2 one observes that one can even obtain a saturation of the extra resonances. This result is also obtained theoretically for long relaxation times of the order of a second. It is to be noted that it is not possible to evaluate the relaxation time from the saturation curve in Fig. 2 applying, for instance, Castner's theory[7] because in our experiment a magnetic field modulation technique is used giving rise to a fast-passage mechanism because of the long relaxation time of the center[8] and in such case, Castner's theory is not relevant.

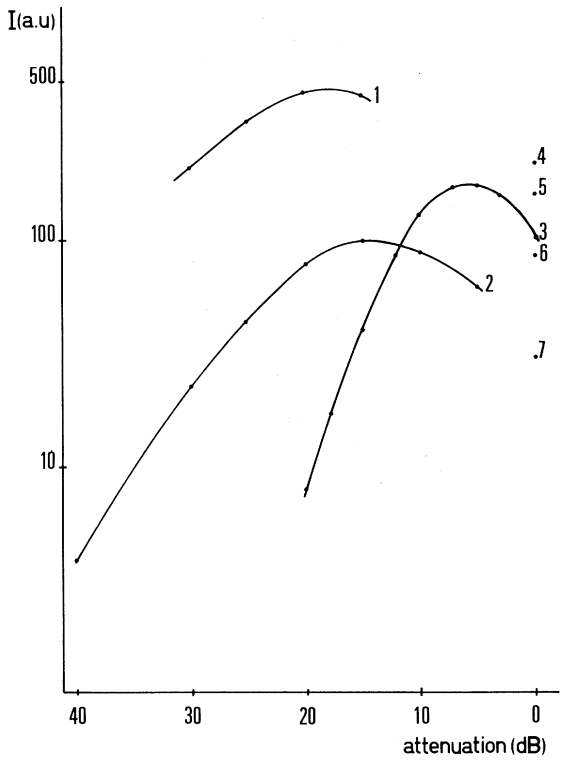

FIG. 2. Saturation curve of the different EPR lines; the numbers refer to n.

If one considers only the component of $\vec{H}_1$ perpendicular to $\vec{H}$, the calculations become much simpler and one can obtain approximate analytical expressions for the homogeneous absorption EPR signal v near resonance. Of course in such a case one can only explain the odd resonances because of the conservation of angular momentum. With the help of Stenholm's calculations,[9] we obtain

$$v=\frac{(2p+1)[(\gamma H_1)^{4p+1}/(4\omega)^{4p}(p!)^4]\,T_2 M}{1+\{[(2p+1)\omega-\delta\omega-\gamma H]T_2\}^2+[(\gamma H_1)^{4p+2}/(4\omega)^{4p}(p!)^4]\,T_1 T_2},$$

where $2H_1$ is the zero-to-peak amplitude of the microwave magnetic field, $\omega/2\pi$ the microwave frequency, T_1 and T_2 the longitudinal and transverse relaxation times; M is the static magnetization $[M\simeq(2p+1)\chi_0 H_0]$ and $\delta\omega$ is the Bloch-Siegert shift of the resonance; to first order

$$\delta\omega=(\gamma H_1)^2/4\omega \quad \text{for } p=0, \qquad \delta\omega=[(\gamma H_1)^2/4\omega](2p+1)/p(p+1) \quad \text{for } p=1,2,3\ldots.$$

In this expression one can see that the saturation condition for the $(2p+1)$th resonance is

$$[(\gamma H_1)^{4p+2}/(4\omega)^{4p}(p!)^4]\,T_1 T_2 \sim 1.$$

In diluted systems as it is the case in the present study, one has $T_2 = T_1$ and the saturation condition becomes

$$[(\gamma H_1)^{2p+1}/(4\omega)^{2p}(p!)^2]\, T_1 \sim 1.$$

One can see that at X-band frequencies and for H_1 of the order of 1 G, saturation of an homogeneous line is obtained for T_1 of the order of several seconds.

Quantitative comparisons between Fig. 2 and our calculations are not possible for several reasons. The first one is that our experiments are made in fast-passage conditions because of the modulation and our calculations do not take this effect into account; the second one is that we are dealing with inhomogeneous lines and our calculations concern individual spin packets. Finally $\vec{H}_1$ in our experiment is strongly inhomogeneous and is not a well known quantity. But it seems clear from these calculations that the physical reason for the observation of the $n > 1$ resonances is a long relaxation time of the center.

We shall now discuss whether a relaxation time of the order of a second at 3.5 K is reasonable for the Cr^+ center in GaP. Cr^+ is an S-state ion which are known to have long relaxation times. One should remark that the Cr^+ charge state is -2 compared to the gallium lattice charge. As a consequence Cr^+ has a tendency to repel the ligand orbitals leading to a weak overlap between the Cr^+ and ligand orbitals which induces a long relaxation time of the center. This fact explains why such extra resonances have not been previously observed in the study of S-state ions for instance in the study of Mn^{2+} or Fe^{3+} in II-VI or III-V compounds; in these last cases the relaxations times are shorter than in the case of Cr^+ in GaP. For instance, at X-band frequencies, the relaxation time has been measured to be 0.01 s at 3.5 K in the case[10] of substitutional Fe^{3+} in ZnS (charge +1 compared to the lattice charge) and 0.3 s at 3.5 K in the case[11] of substitutional Mn^{2+} in ZnS (charge 0 compared to the lattice charge). The relaxation time of interstitial Cr^+ in silicon is 3 s at 3.5 K.[12] Extrapolated from these last results, a relaxation time of several seconds for Cr^+ in GaP at 3.5 K seems very plausible. The observation of multiphoton resonances in this case is thus consistent with the Bloch equations.

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