

only when all possible sources of error are understood, and to date we do not believe this to be the case.

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¹B. W. Batterman, Phys. Rev. Lett. **2**, 47 (1959).

²D. Chipman (private communication).

³D. R. Hartree (private communication).

INVERSION OF PARAMAGNETIC RESONANCE LINES IN IRRADIATED CALCITE*

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Spin-lattice relaxation times as long as three minutes have been observed for radiation-induced paramagnetic resonance lines in calcite at 1.6°K. At 77°K the corresponding time is 5 milliseconds.

Resonance was observed with a conventional superheterodyne bridge spectrometer operating at 9 kMc/sec.¹ Samples were cut from reasonably clear natural calcite crystals and ground to fit rectangular X-band waveguide. Their lengths were adjusted to be resonant at the desired frequency; no iris was used.

Irradiations were performed with 3-Mev electrons. Measurements on one crystal indicated that a dose of 60 microcoulombs/cm², administered in two separated 30-second periods, produced ~10¹⁷ paramagnetic centers/cm³ of the type which contributed to the strongest line.

This spin density was measured by comparison with a crystal of copper-doped zinc Tutton's salt of known copper concentration. The above dosage rate caused the crystal to heat appreciably, and lower rates were found to be more efficient in producing centers. The centers fade in a few hours at room temperature and in a few days at liquid nitrogen temperature.

Several of the crystals, both before and after irradiation, exhibited a number of relatively weak lines which were identified as the spectrum of Mn⁺⁺, present as an impurity in the calcite.

The positions and intensities of these lines agreed exactly with the work of Hurd *et al.*,² and served as a convenient calibration for the radiation-induced lines.

At least seven additional lines appeared as a result of irradiation. These are listed in Table I for a typical run on a crystal cut so that its optic axis is parallel to the static magnetic field ($\theta = 0^\circ$). All Mn⁺⁺ lines would be classified as "weak" or "very weak" on the scale of relative intensities used in the table. The strongest line (3271 gauss) exhibits a g value of 2.00, constant with changing radio-frequency and nearly constant with changing θ . The other lines change considerably with both frequency and θ .

Inversion of the various lines has been accomplished by adiabatic fast passage, using both field and frequency sweeps. Spin-lattice relaxation times (T_1) were measured by observing the rate of decay of the inverted absorption signal back toward its equilibrium value. Measured T_1 values at 1.6°K for five of the irradiation-induced lines are listed in Table I. Inversion of the other lines in the table was not attempted. An effort to invert a few of the larger Mn⁺⁺ lines was unsuccessful, indicated $T_1 < 1$ second for these lines.

The relaxation times shown in Table I are probably somewhat smaller than the true values, for two reasons. First, the strength of the lines is so large that it is extremely difficult to avoid saturating the lines with the microwave power ($< 10^{-12}$ watt) used for observation. Further reduction of this power was impossible because of system noise, originating principally in the detector. Second, the inverted spin system reduced the loaded Q of the cavity appreciably, causing regeneration and an artificially rapid decay. This effect was minimized for T_1 measurements by using low- Q cavity modes and by

Table I. Resonance lines caused by irradiation in CaCO₃. Radio-frequency 9155 Mc/sec, $\theta = 0^\circ$.^a

Relative intensity	Magnetic field (gauss)	T_1 at 1.6°K (min)
Strong	4620	3
Medium	3950	
Strong	3406	1
Weak	3288	
Very strong	3271	1
Weak	3245	2
Strong	2410	3

^aThe first, second, and last lines in the table were outside the range of the proton resonance magnetometer. Magnetic fields for these lines were estimated from the magnet current readings.

broadening the resonance line with a slightly inhomogeneous field.

Complete inversion of the irradiation-induced lines was possible at frequency sweep rates as low as 2×10^{10} cycles/sec² using 0.1 watt of rf power. Thus the transverse relaxation time (T_2) is greater than 10^{-4} sec for these lines. Observed line widths were about one gauss, corresponding to T_2^* of the order of 10^{-7} sec, so the lines have appreciable inhomogeneous broadening.

No evidence was found for a two-stage spin-lattice relaxation process, as proposed by Townes.³ In every case, the inverted lines decayed through the zero signal (equal population) configuration without observable change of rate.

Crystals which received the same $60\text{-}\mu\text{coul/cm}^2$ dose distributed over a four-minute period exhibited only a single, very strong resonance line, three gauss wide, centered at $g=2.00$, and apparently made up of several nonresolved components. The value of T_1 for this line at 1.6°K was still several minutes, even though some spin-spin interaction was evidently involved. Relaxation-time measurements were also made on such a crystal at liquid nitrogen temperature, using a frequency-sweep system. The observed T_1 was 5 ± 1 milliseconds, and the limits on fast passage indicated that T_2 was greater than 10^{-6} sec.

The extremely long spin-lattice relaxation time found in these experiments makes irradiated calcite a desirable material for use in two-level solid state maser oscillators and amplifiers. Spontaneous oscillations were observed on several occasions during the measurements at 1.6°K described above. Controlled oscillations were later obtained with a maximum power output of the order of 10^{-8} watt. An amplifier was then constructed by incorporating a ferrite circulator into the spectrometer to separate the input and output signals. Gains of 20 db and greater were observed at liquid helium temperature, and by progressively increasing the magnetic field homogeneity after inversion, amplification could be maintained for several seconds. The $(\text{gain})^{1/2}$ -bandwidth product was not measured directly, but a value of 6×10^7 sec⁻¹ would be expected theoretically for 10^{17} spins/cm³ with $T_2^* = 10^{-7}$ sec. Although there were not enough spins in the crystal to produce oscillation or amplification at liquid nitrogen temperature, it seems quite possible that a sufficiently large spin density might be achievable without excessive shortening of the relaxation times.

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¹See, for example, G. Feher, Bell System Tech. J. **36**, 449 (1957).

²Hurd, Sachs, and Hershberger, Phys. Rev. **93**, 373 (1954).

³Giordmaine, Alsop, Nash, and Townes, Phys. Rev. **109**, 302 (1958).

DIAMAGNETISM OF CONDUCTION ELECTRONS IN METALS

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The calculation of the diamagnetic susceptibility of the conduction electrons has long been one of the most troublesome problems in the one-electron theory of metals. When the electrons can be treated as free the calculation is relatively simple,¹ but when the periodic lattice potential is introduced it is found that virtual interband transitions make a non-negligible contribution to the total susceptibility, and this greatly complicates the analysis. The problem has been discussed a number of times²⁻⁴ since the original work of Peierls on the subject,⁵ but no complete and really satisfactory treatment seems to have been given so far.⁶ In a re-examination of the problem we have found that the field-independent part of the susceptibility can, in fact, be calculated exactly and put into a reasonably simple form. The method of calculation follows established lines,³ and amounts to the determination of the term proportional to H^2 in the expansion of $\text{Tr}[\exp(-\mathcal{H}/kT)]$ in ascending powers of H , where \mathcal{H} is the Hamiltonian of an electron in the periodic lattice potential and a constant external magnetic field H (assumed to be in the z direction). The trace is formed by using as basis the