Saturation and Recovery of a Portion of the Electron Spin Resonance of *F* Centers in KCl at 4°K

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The inhomogenously broadened magnetic resonance of *F* centers in additively colored potassium chloride was photographed using a field modulation which swept rapidly across the resonance as the absorption was displayed on the oscilloscope. The time between sweeps was long and adjustable. A concentration dependence of the spin lattice relaxation time was observed at 4.2°K. In crystals with a concentration near 1×10^{17} cm^{-3}, a portion of the resonance could be saturated without affecting the rest of the broad spectrum. The recovery time of this "hole burned in the resonance" is about a quarter of a minute. The results are compared with present theories on spin diffusion.

THE electron spin paramagnetic resonance of *F* centers in potassium chloride is inhomogeneously broadened by the unresolved nuclear hyperfine splitting. This system has a wide and continuous distribution of spin states which are easily saturated. One may increase the concentration of unpaired electrons to 7×10^{-4} per potassium ion. This makes the colored crystal an excellent system in which to study spin-spin and spin-phonon interactions. Several discussions of the theoretical aspects of these interactions have been presented.[1–5]

At 4°K the resonance saturates even when 10^{-5} watt of microwave power is incident on a sample cavity with a Q of 3000. These experiments show that at concentrations less than 7×10^{-5} *F* center per potassium ion a portion of the resonance may be saturated independently of the remainder. Further, the width of the saturated region indicates that there is very limited transfer of magnetization from spins resonating at one field to those at a higher or lower field. These experiments resemble the burning of holes in the resonance of protons in an inhomogeneous external field.[6] Our experiments on electron spins are done in a very homogeneous magnetic field and the different local fields are caused by the many possible orientations of the surrounding nuclei. The geometric distance between electrons of different resonant frequencies is small enough that the possibility of spin diffusion exists.

The resonance was observed using the magnetic resonance spectrometer described previously.[7] The 9.0 kMc frequency was stabilized on the sample cavity. The klystron was operated at reduced voltages and up to 50-db attenuation was available between it and the magic tee. The superheterodyne detector was coupled to the y axis of an oscilloscope. The voltage on the x axis of the oscilloscope was derived from the current through the field modulation coils. The magnetic field was set to saturate a portion of the resonance for an indefinite time. The field was then moved off resonance and periodically swept across it. This trapezoidal wave field modulation was produced by an electronic circuit which closed and periodically reversed the connections of the modulation coils to a dc supply. The observation of the resonance was fast and infrequent so it did not cause saturation. The shortest time between sweeps was 34 milliseconds. A sweep of 175 gauss occurred linearly in 7 milliseconds over the initial 150 gauss. The microwave field was left on continuously.

The samples were colored additively and the concentration was uniform. The crystals were quenched in oil and handled completely in the dark. This produces pure *F* centers.[8] The concentrations were obtained from optical absorption measurements or the coloring temperatures.

Figure 1 shows the resonance observed after the center of the absorption spectrum was saturated. This sample has about $7\times10^{-6}F$ center per potassium ion. Very little change takes place between sweeps across the resonance and the recovery time is greater than 10 sec. Samples with this lower concentration have repeatedly shown a small peak at the bottom of the hole. Figure 2 shows the recovery of the hole in a second crystal which is about four times as concentrated. The time for half-recovery soon after saturation is shorter than the six seconds for half-recovery as the system approaches equilibrium. In

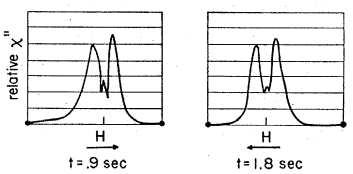

FIG. 1. The absorption observed 0.9 and 1.8 sec after saturation of the center of spectrum at 4°K. The resonance was displayed on the oscilloscope and photographed. The high frequency field, H_1, was about 4.8×10^{-4} gauss. The concentration was 1.1×10^{17} cm^{-3}.

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a third sample with a concentration ten times the first, the initial trace showed that a portion of the resonance is saturated but recovers within 0.03 second. In all crystals the trace made, as the field moves off resonance after the saturation, indicates a saturated width of several gauss. In the time the field remains off resonance the hole becomes less deep and about 10 gauss wide.

The external magnetic field inhomogenity, the microwave frequency fluctuation, and the bandwidth of the detection system do not account for the observed width. During the initial saturation, the rf power remains on the center of the resonance for a time which is sufficient for spin diffusion to take place. However, there is no change in the unsaturated region so the energy does not diffuse into the tails during the initial saturation or the later recovery.[5] The width of the saturated region is greater than the width of an individual multiplet (theoretically less than 1 gauss) indicating spin diffusion. The width of the saturated region is limited by the competition between spin diffusion and spin-lattice relaxation. A quantum of energy in the F center may either be exchanged with a neighbor or be absorbed by the lattice. The probability of energy transfer to a frequency neighbor is proportional to the difference in saturation at the two frequencies. The relaxation is proportional to the saturation. Spread of the saturation ceases when the gradient of the population difference is such that energy is transferred to the lattice before it diffuses to an unsaturated neighbor.

The concentration does not have a large effect on the width of the hole but the recovery rate is roughly proportional to the concentration. The recovery rate in the most dilute crystals is taken as a measure of the spin-lattice relaxation time, T_1. This may, however, still represent the time for heat conduction from the region of the F center and not the time which might be calculated for transfer of energy from spins to phonons. The hole has not been observed at 78°K so the large change in recovery time occurs above 4°K. The phonons in potassium chloride corresponding to the appropriate spin energy do not have an electromagnetic field associated with them. Therefore, the author believes that the spin interacts with two or more optical phonons instead of directly with one acoustical phonon.

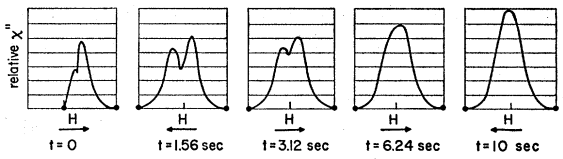

FIG. 2. A sequence of tracings made from a single photograph showing the recovery of the saturated portion of the resonance absorption at 4°K. The high-frequency field was 4.4×10^{-4} gauss. The sweep is 156 gauss between extremes and the center of the trace is near 3200 gauss. The concentration of F center was 4.8×10^{17} cm^{-3}.

The small peak in the bottom of the hole in the resonance observed in crystals of low concentration is possibly caused by cross relaxation.[4] Two saturated spins can exchange energy with two other spins having the same total energy. However, the process cannot proceed farther because of the absence of unsaturated pairs of systems whose absorption sufficiently overlaps that of the saturated systems.

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Transverse Collective Excitations in Superconductors and Electromagnetic Absorption*

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With use of the generalized random phase approximation an attempt is made to estimate the absorption of photons with energy less than the energy gap due to transverse collective excitations. The ratio of the surface resistance due to transverse collective excitations to that of normal metals in the extreme anomalous limit, calculated within the weak coupling theory, turns out to be too small to explain the observed data for superconducting lead and mercury. The interpretation of the collective excitations as bound pair states is briefly discussed.

I. INTRODUCTION

RECENTLY Ginsberg, Richards, and Tinkham measured the absorption of infrared radiation in bulk samples and the transmission through thin films of several superconductors.[1] The observed data were in good agreement with the result of the theory of Mattis and Bardeen, except for an interesting anomaly in the case of superconducting lead and mercury. For these

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