Saturation Effects in Moderately Diluted Cesium Chromium Alum*

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(Received December 8, 1961)

The steady-state saturation method was used to investigate the paramagnetic relaxation of the chromium ion in cesium chromium (aluminum) sulfate at 24 kMc/sec and at liquid-helium temperatures. The relaxation behavior was studied as a function of the intensity of the microwave field, the temperature, the magnetic-ion concentration, and the spin transition. For the power range used, a single relaxation parameter was found adequate to describe the saturation behavior. The Cr/Al ion concentration was varied between 1/0 and 1/93. For each of the spin transitions investigated, it was found that the relaxation parameter increased with magnetic dilution. For all of the samples tested, the temperature dependence of the relaxation parameter T_1 in the range 1.6° to 4.2°K could be expressed by the relation $T_1T=$const. The results suggest that for these samples the direct process spin-lattice interaction is the dominant energy bottleneck and that more energy-transfer paths are available at the higher magnetic concentrations.

INTRODUCTION

A WIDE variety of experimental results in the field of electron paramagnetic resonance have been reported and attempts to account theoretically for the wide diversity of the data have resulted in a number of proposals concerning possible relaxation processes. Because well-resolved transitions are necessary to measure true spin-lattice relaxation times, the major emphasis of the experimental work has been with regard to highly diluted paramagnetic samples. However, previous steady-state saturation work[1] on moderately diluted salts was interesting not only because the temperature dependence of the relaxation parameters indicated that a spin-lattice process was the dominant energy bottleneck, but also because there were some indications that there were magnetic-concentration and spin-transition dependences that could not be accounted for by the theory involving a true spin-lattice process.

Recently, Bolger,[2] using steady-state saturation methods, studied several moderately diluted salts in detail. Although his work was concerned mainly with nonlinearities in the saturation graphs, that is, with relaxation times dependent on the degree of saturation, he found dilution dependences in several chromium salts that agreed rather well with the previous unexplained results.

Inasmuch as some of these saturation data can now possibly be interpreted in terms of one of the more recent relaxation theories, that is, cross relaxation,[3] it was decided to investigate a moderately diluted chromium salt. In the present experiment steady-state saturation techniques were used to investigate the relaxation parameters of cesium chrome alum as a function of incident microwave power, temperature, magnetic concentration, and spin transition.

* This work was supported by the Office of Naval Research.
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THEORY AND EXPERIMENT

In a magnetic resonance experiment power absorbed by the spins is transmitted to the lattice after a delay in time, and then to the constant-temperature bath. This two-step process requires that a complete description of the relaxation mechanism involve at least two relaxation parameters,[4] the spin-lattice and lattice-bath relaxation times. However, if one of these two processes dominates, a single parameter may be an adequate description of the saturation, inasmuch as only one bottleneck of the energy transfer, the slower one, will be experimentally detectable by saturation methods. The inability of the steady-state saturation method to distinguish directly the dominant energy bottleneck in a multiple relaxation process is a distinct disadvantage, but a study of the relaxation parameter as a function of microwave power, temperature, concentration, and transition can give important information regarding possible relaxation processes.

The theory of steady-state saturation has been described in detail elsewhere.[1,5,6] In a multi-level system, as shown in Fig. 1, the saturating power is applied to essentially one spin transition at a time. If magnetic-dipole transitions alone are important, the steady-state rate equations can be solved for the spin population

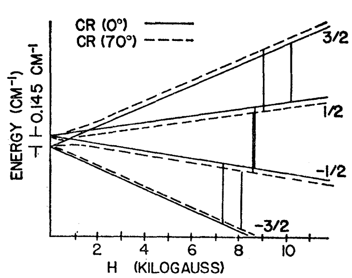

FIG. 1. The possible spin transitions for cesium chrome alum at 24 kMc/sec. The magnetic field is normal to the (111) face of the crystal.

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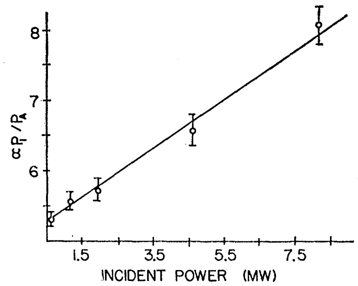

FIG. 2. Typical saturation graph for cesium chrome alum. (Cr/Al: :1/2.4—high-field line—4.2°K).

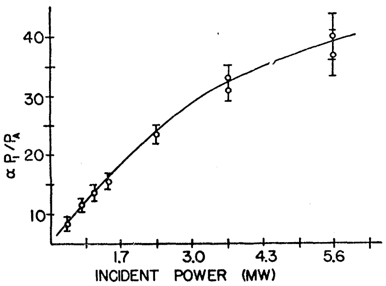

FIG. 3. Saturation graph for undiluted copper ammonium Tutton salt at 4.2°K.

difference $N_{ij}=n_i-n_j$ to give

$$N_{ij}=\frac{N_{ij}^0}{(1+2W_{rf}/Q)},$$

where N_{ij}^0 is the equilibrium population difference and W_{rf} is the rf transition probability per unit time. The quantity Q is related not only to the spontaneous transition probabilities per unit time w_{ij} and w_{ji} (for those levels which are influenced directly by the microwave power), but also to the transition probabilities for all of of the possible spin transitions.[7,8] Thus, $1/Q$ is not the time constant governing the return to equilibrium of a single pair of spin levels, but it is instead that parameter which may be used, in a formal way, to describe the saturation behavior. It is the parameter $1/Q=T_1$ which is measured in the present experiment.

Typical saturation-type spectrometers have been described in detail elsewhere.[1,2] The present work was carried out at a frequency of 24 kMc/sec. Figure 1 shows the locations of the spin transitions of cesium chrome alum for this frequency with the external magnetic field perpendicular to the (111) face of the crystal. The $\theta=0°(-1/2\rightarrow-3/2)$, $\theta=70°(-1/2\rightarrow-3/2)$, and the $\theta=0°(3/2\rightarrow1/2)$ transitions were studied in samples with Cr/Al ion concentrations of 1/0, 1/2.4, 1/6.4, 1/47, and 1/93 as determined by chemical analysis. The microwave power was varied from 10 μw to 12 mw. The relaxation parameters were measured in the temperature range 1.6° to 4.2°K.

RESULTS

When the microwave circuit characteristics remain constant, the microwave field at the sample site is proportional to the square root of the incident power. It is then possible to determine the relaxation parameter, in part, from a saturation graph; that is, a plot of P_I/P_A vs P_I, where P_I is the power incident on the resonant cavity and P_A is the power absorbed by the paramagnetic sample on magnetic resonance. The saturation graphs for all of the cesium salts were straight lines for the power range used. A typical saturation graph for cesium chrome alum is shown in Fig. 2. Bolger[2] has investigated a variety of copper Tutton salts by steady-state methods at 9400 Mc/sec. He found that the saturation graphs, plotted over a sufficiently wide power range, were not straight lines. Furthermore, the curvature was most noticeable at easily obtainable power levels of the order of several milliwatts. Two copper Tutton salts were tested with the present spectrometer. The saturation graphs for the $CuNH_4$ and CuK Tutton salts are shown in Fig. 3 and Fig. 4. There is a marked change in slope at about 2 mw. A detailed study of the copper salts was not made and direct comparison of the data is difficult inasmuch as the copper salts show a marked size dependence. It should be pointed out that Bolger has detected curvature in the saturation graphs for several chromium samples. However, Fig. 2 indicates that for the samples and range of power used in this experiment, a single relaxation parameter is an adequate description of the saturation behavior for cesium chrome alum.

Previous relaxation data had indicated that the temperature dependence of the relaxation parameter could be expressed by the relationship $T_1T^n=$constant.[1,9] This relationship could be satisfied in the present work. The average value of n for the 5 chromium samples was 1.0 ± 0.1. The value of n did not depend on either the magnetic concentration or the spin transition.

In contrast, the data listed in Table I shows that the magnetic concentration and spin transition did affect the value of T_1. Figure 5 shows the concentration dependence of the relaxation rate of the $\theta=0°$, $(-1/2\rightarrow-3/2)$, transition at 4.2°K.

DISCUSSION

The linear saturation graphs for the cesium chrome alum samples make it possible to calculate, unambigu-

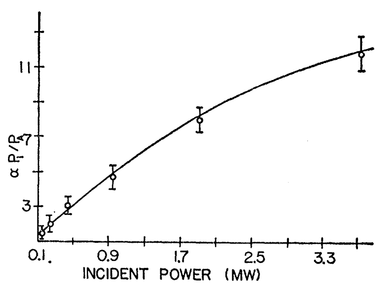

FIG. 4. Saturation graph for undiluted copper potassium Tutton salt at 4.2°K.

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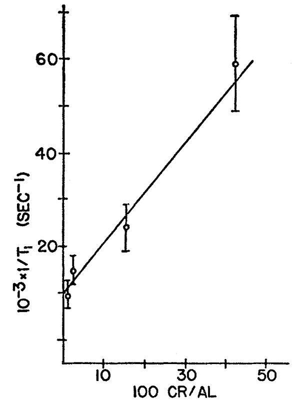

FIG. 5. The concentration dependence of the relaxation rate of the $\theta=0°$ $(-1/2\rightarrow -3/2)$ transition for cesium chrome alum at 4.2°K.

ously, a single T_1 for each transition over the range of power used here. Relaxation in the copper salts can not, however, be characterized by a single power-independent parameter.

The $1/T$ temperature dependence of T_1, which agrees with previous saturation data on chromium salts, indicates that the dominant energy bottleneck in this temperature range is the direct spin-lattice process.

TABLE I. The magnetic concentration and spin transition dependence of the relaxation parameter T_1 for cesium chrome alum at 4.2°K. The magnetic field is perpendicular to the (111) face of the crystal.

Concentration (Cr/Al)	Spin transition	T_1 (10^{-5} sec)
1/0	i: $\theta=0°(-1/2\rightarrow -3/2)$	1.4
1/0	ii: $\theta=70°(-1/2\rightarrow -3/2)$	0.9
1/0	iii: $\theta=0°(3/2\rightarrow 1/2)$	1.3
1/2.4	i	1.7
1/2.4	ii	1.0
1/2.4	iii	1.8
1/6.4	i	4.3
1/6.4	ii	1.6
1/6.4	iii	4.0
1/47	i	6.7
1/47	ii	5.3
1/47	iii	7.7
1/93	i	11
1/93	ii	7.7
1/93	iii	16

Because the direct process depends only on the interactions between the spins and the lattice, this direct process should yield a relaxation parameter which is not dependent on the concentration of the paramagnetic ion. Table I and Fig. 5 show that T_1 is dependent upon magnetic concentration. This dependence of longer relaxation parameters for greater magnetic dilution can be interpreted on the basis of the cross relaxation process. This interpretation is compatible with the temperature dependence. Greater dilution reduces the cross relaxation process which lowers the total number of energy transfer paths, but in all cases the dominant energy bottleneck is the direct spin-lattice process.

Three different spin transitions were studied in order to better determine the effect of cross relaxation. If cross relaxation is responsible for the concentration dependence, it is possible that T_1 is shorter for the $\theta=70°(-1/2\rightarrow -3/2)$ transition than for either the $\theta=0°(-1/2\rightarrow -3/2)$ or $\theta=0°(3/2\rightarrow 1/2)$ transition inasmuch as the former can cross relax very easily with both the low-field line and the strong central peak, while the latter two transitions are more removed from the central peak and have neighboring lines on only one side. Table I shows that the values of T_1 measured here are consistent with this interpretation; that is, T_1 is less for the $\theta=70°$ transition than it is for the other two lines.

There are two other much less pronounced suggestions in the data that can be explained in the above terms. At low dilutions the T_1 for the high-field and low-field lines are approximately equal; however, as the dilution increases, the T_1 for the high-field line becomes measurably longer. Also, the recovery rate of the 70° transition does not change as rapidly as the rate for the other two transitions when the concentration is varied from 1/0 to 1/6.4. The first effect can be interpreted in terms of the greater isolation of the high-field line; the second effect is plausible because very moderate dilution will begin to resolve the high- and low-field lines rather well, but the $\theta=70°(-1/2\rightarrow -3/2)$ transition will not be resolved as yet from the strong central peak. There are, therefore, strong indications that this and some of the other low-power saturation data are consistent with the cross relaxation and direct spin-lattice process theories.