MEASUREMENT OF THE SPIN-LATTICE RELAXATION TIME IN COMPOUNDS WITH STRONG COVALENT BONDING

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The spin-lattice relaxation time T_1 for Fe^{3+} and Cr^{3+} ions in $K_3(Fe, Cr)(CN)_6$ was measured by the methods of pulsed and continuous saturation. For Fe^{3+} concentrations of 0.1 and 0.21% the relaxation time T_1 was found to be independent of concentration in the temperature range from 2.1 to 40°K and equal to $0.64\ T^{-5}$ sec. The experiment shows in a qualitative way that there is a strong cross relaxation between the lines from the two non-equivalent ions. The measurements of T_1 for Cr^{3+} also indicate the existence of cross relaxation.

INTRODUCTION

THE study of spin-lattice relaxation has received a new impetus in connection with the development of quantum paramagnetic amplifiers. Several series of experiments[1-4] on spin-lattice relaxation point to an anomaly which cannot be explained by the existing theory. Some effects observed in the work of Giordmaine et al.[3] were explained by the existence of cross relaxation.[5] We wished to study spin-lattice relaxation in the simplest system having two levels without hyperfine structure.

For this purpose we chose Fe^{3+} ions in the compound $K_3Fe(CN)_6$ with strong dilution by Co^{3+} ions. Because of the considerable convalent bonding the Fe^{3+} ion has an effective spin $S = \frac{1}{2}$.

We studied crystals with different relative concentrations of Fe and Co, namely 1:1000 and 2.1:1000. Baker et al.[6] have studied the spectrum of $K_3Fe(CN)_6$ at T = 20°K. They showed that there are two magnetically non-equivalent Fe^{3+} ions and gave the values of the g factors. In our experiments we aimed to have the lines from the two non-equivalent ions coinciding.

We used both the continuous saturation and the pulse methods to investigate spin-lattice relaxation.

Figure 1 shows the block diagram of the spectroscope used. The klystron K_1 operated under pulsed conditions, giving 25 μsec pulses with a rise time of < 1 μsec at a repetition rate of 100 to 0.1 cps. The power of 1.5 w in the pulse was quite sufficient to achieve appreciable saturation during the period of the pulse. The rest of the apparatus consists of a superheterodyne spectroscope working on the low power level of the signal klystron K_2 at a
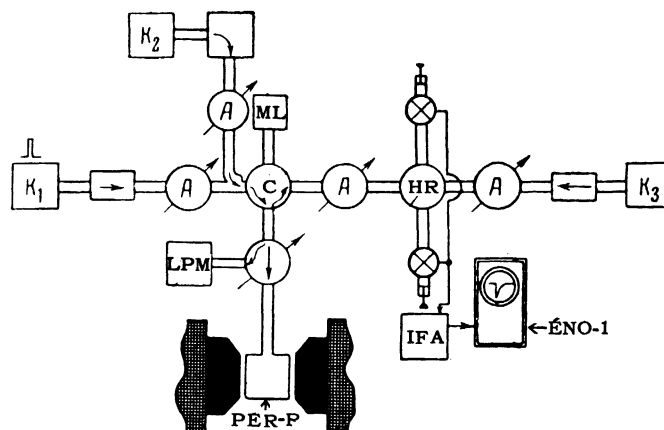

FIG. 1. Block diagram of spectroscope for measuring the spin-lattice relaxation time by the pulse method. K_1, K_2, K_3 — klystrons. A — attenuator. LPM — lower power meter. ML — matched load. C — circulator. HR — hybrid ring. R — resonator. IFA — intermediate frequency amplifier. ÉNO-1 — oscillograph.

frequency of 9400 Mc/sec. For measurements by the continuous saturation method, klystron K_1 operates under CW conditions and the power at which saturation is reached is fed to the power measurer LPM through the waveguide directive feed. A relaxation curve for Fe^{3+} is shown in Fig. 2.

EXPERIMENTAL RESULTS

The spin-lattice relaxation time T_1 at 4.2°K, measured for both Fe^{3+} concentrations by the pulse method, was found to be $(4.9 \pm 0.4) \times 10^{-4}$ sec. The corresponding spin-spin relaxation times T_2 are 1.4×10^{-8} and 0.66×10^{-8} sec. The continuous saturation method, the accuracy of which is lower, gave good agreement with these data. At 2.1°K, T_1 for both concentrations is $(1.6 \pm 0.2) \times 10^{-2}$ sec. Examination of the relaxation curve showed it
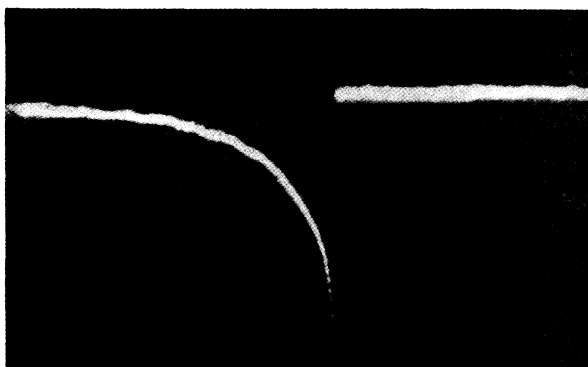
FIG. 2. Oscillogram of relaxation curve of the Fe^{3+} ion.

to be exponential with a single characteristic time, as expected for a two-level system.

It follows that at helium temperatures the spin-lattice relaxation time is independent of concentration for the Fe^{3+} ion concentrations studied, and is inversely proportional to the fifth power of the temperature. Such a strong temperature dependence of T_1 indicates that second-order processes are dominant at liquid helium temperatures. We measured the line width for the 0.21% specimen between 4.2 and 40°K to check the temperature dependence of T_1 at higher temperatures. Between 2.1 and 19°K the line width does not change, showing the small contribution of spin-lattice interaction to the line width. The width rapidly increases above 20°K, owing to the decrease in T_1 and the corresponding contribution of spin-lattice interaction to the overall line width. The relaxation time T_1 calculated from the line width also follows a T^{-5} law up to 40°, where the line is very strongly broadened and becomes difficult to observe.

Thus from 2.1 to 40°K, T_1 is independent of concentration and is given by

$$T_1 = 0.64\, T^{-5} \quad \text{sec}.$$

A preliminary study by the pulse method of the influence of cross relaxation between the two lines from non-equivalent ions did not yield results. This is probably due to the short cross-relaxation time. We therefore carried out another experiment to determine qualitatively whether there is cross relaxation in the present case. For this, a specimen with a Fe^{3+} ion concentration of 0.46% and 24 oe line width was placed in the resonator in which two types of wave were excited, differing in frequency by 300 Mc/sec (reference 2). The specimen was oriented in such a way that the distance between the lines from the two non-equivalent ions was also 300 Mc/sec, so that both lines were observed simultaneously on two spectroscopes on modulating the frequency. One of the lines was saturated and

the behavior of the other studied. At the orientation mentioned, when the distance between the lines was approximately four line widths, the lines are saturated together.

It requires a much larger power to achieve an analogous saturation of the line using a klystron at the same frequency difference. This indicates the existence of cross relaxation.

We also carried out a preliminary study of the relaxation processes in $K_2Cr(CN)_6$ with a 0.24% Cr^{3+} concentration. The constant magnetic field was directed along the z axis in the crystallographic ac plane and the $2 \leftrightarrow 3$ transition was studied by the pulse method. It appeared that the relaxation curve at 4.2 and 2.1°K can be represented quite accurately by the sum of two exponentials with very different relaxation times. One exponential time is independent of temperature and is 4.5×10^{-4} sec, while the other is inversely proportional to temperature and is 1.9×10^{-3} sec at 4.2°K. We are certainly concerned here with cross relaxation, the existence of which was indicated in earlier work.[2,4,7,8] Such a rapid cross relaxation is evidently connected, on the one hand with the fairly large concentrations and on the other with the fact that for the given orientation the frequency of the $3 \leftrightarrow 4$ transition is almost exactly half the frequency of the $2 \leftrightarrow 3$ transition. The pulse method, using short saturating pulses, can certainly give much more information about rapid cross relaxation processes than a method using long pulses.

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