RELAXATION PROCESSES IN THE PARAMAGNETIC RESONANCE OF Gd^{3+} *IN* CaF_2

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The relaxation processes of Gd^{3+} ions in the fluorite lattice were studied at 9370 Mc/sec and liquid helium temperature by the pulse saturation method. The relaxation times were determined for Gd^{3+} in crystal fields of various symmetries. The relaxation times for ions in a tetragonal or trigonal field depend weakly on temperature. The absence of a concentration dependence of the spin-lattice relaxation time is discussed. Spin-spin cross-relaxation times were measured at concentrations of 3×10^{-4} and 5×10^{-4}. The cross-relaxation effects are discussed.

1. INTRODUCTION

RECENTLY a number of theoretical papers have appeared on the mechanism of spin-lattice relaxation of S-state ions.[1,2] However, the experimental data are inadequate to form definite conclusions about which of the various types of spin-lattice interaction predominate for these ions. In this connection it is of interest to investigate the relaxation processes of Gd^{3+} ions. The spin-lattice relaxation of Gd^{3+} ions has previously been studied in ethylsulfate[3-5] and SrS[6] crystals.

We have studied the relaxation processes in the paramagnetic resonance of this ion in CaF_2. Crystals of CaF_2 are of particular interest because in them it is possible to obtain the Gd^{3+} ion in crystalline electric fields of various symmetries (cubic, tetragonal, and trigonal).[7-9] Thus in this case we have the possibility of examining the effect of crystal field symmetry on spin-lattice relaxation of a given paramagnetic impurity ion in a given host lattice.

We might also point out that the case of Gd^{3+}, which has a large number of spin levels ($2S + 1 = 8$), is interesting because we can study the character of spin-spin cross-relaxation in a multilevel system.

2. EXPERIMENTAL CONDITIONS

The experiments were carried out at 9370 Mc/sec and at helium temperatures. The pulse saturation method was used. In order to distinguish the spin-lattice relaxation and spin-spin cross-relaxation processes from each other, the saturating pulse length was varied from 40 μsec to 50 msec. The concentration of Gd in the samples was varied from 10^{-5} to 10^{-3}, representing the relative number of Gd ions replacing Ca ions in the CaF_2 lattice and determined from the composition of the initial mixture.

The samples studied contained Gd^{3+} in crystal electric fields of cubic, tetragonal, and trigonal symmetry. The relaxation times were measured for the spectral lines obtained with the magnetic field in the following orientations: H ∥ [100] and H ∥ [111]. In CaF_2 monocrystals there are three magnetically unequivalent ions in tetragonal symmetry (when H ∥ [111] all these ions become equivalent and give coincident EPR spectra). In the case of trigonal symmetry there are four magnetically unequivalent ions (when H ∥ [100] all these ions become magnetically equivalent).

3. EXPERIMENTAL RESULTS AND DISCUSSION

The relaxation time was measured from the relaxation curve of the restoration of the intensity of the absorption line after the saturating pulse. For concentrations of Gd less than 10^{-4} the relaxation curve is described by a single exponential, within the limits of experimental error. For higher concentrations the curves are described by a sum of two exponentials. The contributions of the individual exponents depend to a marked degree on the length of the saturating pulse. The typical appearance of the relaxation curves for these two cases is shown in Fig. 1, a and b.

The results of the relaxation time measurements for the various crystal fields and sample orientations are presented in Tables I—III.

These results permit us to draw the following

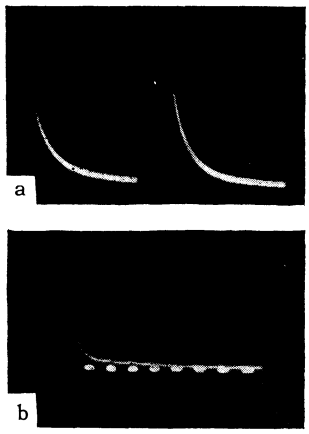

FIG. 1. Relaxation curves for Gd concentration $< 10^{-4}$ (a) and $> 10^{-4}$ (b).

TABLE I. Relaxation times of "cubic" Gd^{3+} ions

$H \parallel [100]$			$H \parallel [111]$		
H, Oe	T_1, msec		H, Oe	T_1, msec	
	4.2°K	1.7°K		4.2°K	1.7°K
2640	19.5	47	3300	23	58
2770	20.5	50			
3275	22	53			
3920	22.5	54			

TABLE II. Relaxation times of "tetragonal" Gd^{3+} ions

$H \parallel [100]$			$H \parallel [111]$		
H, Oe	T_1, msec		H, Oe	T_1, msec	
	4.2°K	1.7°K		4.2°K	1.7°K
1130	17	25	755	20	32
1170	17	28	1930	20	32
2300	20	35	1975	18	30
4420	29	40	3722	29	41

TABLE III. Relaxation times of "trigonal" Gd^{3+} ions

$H \parallel [100]$			$H \parallel [111]$		
H, Oe	T_1, msec		H, Oe	T_1, msec	
	4.2°K	1.7°K		4.2°K	1.7°K
1200	37	46	1030	31	53
1595	58	77	1220	30	46
2075	33	50	2230	31	47
4185	33	51	3360	65	102

conclusions about the nature of the spin-lattice relaxation of Gd^{3+} in CaF_2:

a) Although the line width varies markedly with concentration, the spin-lattice relaxation time in the samples we studied does not, within the limits of experimental accuracy. From a physical point of view, this is an extremely important fact and is probably characteristic of the rare-earth ion.[1)] In the iron-group ions the spin-lattice relaxation time is usually found to be strongly concentration-dependent.[11] This dependence is probably associated with the exchange interactions of the outer 3d electrons.[12] The exchange interactions in the case of rare-earth ions, whose paramagnetic resonance is due to inner 4f electrons, are obviously significantly weakened by the screening effect of the outer electron shells of the ion.

b) The nature of the temperature dependence of T_1 depends essentially on the zero-field splittings of the Gd^{3+} energy levels in the various crystal fields. In the case of the cubic field, T_1 is inversely proportional to the temperature, which indicates a single-phonon relaxation process.

For "tetragonal" and "trigonal" ions and for all observed lines, the dependence of T_1 on the temperature T is weaker than $T_1 \propto T^{-1}$. This can be explained on the basis of an analysis of the temperature dependence of spin-lattice relaxation caused by resonant processes of the first order in multi-level systems with large splittings. Actually, the total splittings of the energy levels of the "tetragonal" and "trigonal" Gd^{3+} ions in CaF_2 exceed the magnitude of kT in the helium temperature region, and the spin-lattice relaxation of EPR lines observed at 9.4 Gc/sec and corresponding to transitions between upper levels can occur via the lower levels. As was shown earlier,[13] this leads to a weak dependence of T_1 on temperature.

c) The spin-lattice relaxation time T_1 depends weakly on the symmetry of the crystal field in the temperature range studied.

As was mentioned above, at Gd concentrations less than 10^{-4}, strong evidence was found for cross-relaxation in all the EPR lines, and the relaxation curves appear as the sum of at least two exponentials with sharply different time constants. The relative weight of the "fast" exponents depends to a great extent on the length of the saturating pulses (from 40 to 95%). The time constants characterizing cross-relaxation are included between the limits of 0.1 and 1 msec. An interesting, unusual cross-relaxation effect was observed in the trigonal case on two lines of the spectrum observed with $H \parallel [111]$ and $T = 1.7°$ K.

For long pulse lengths (50 msec), the relaxation curve had the shape shown in Fig. 2. Such a curve can be qualitatively explained in the following way: When the transition between the energy

[1)] We point out, however, that Pashinin and Prokhorov[10] observed a concentration dependence of T_1 for Yb^{3+} in CaF_2.

levels corresponding to the observed EPR line is saturated, a change in the steady-state population of the other levels of the Gd^{3+} spin system occurs as a consequence of the spin-spin cross-relaxation interactions. After removal of the saturating pulse, the populations of the levels belonging to the observed transition will be redistributed via two paths: 1) via interactions with other levels of the spin system (cross-relaxation) and 2) via transfer of energy to the lattice (spin-lattice relaxation).

If the capacity of the first channel is sufficiently large, then in a time t' less than the spin-lattice relaxation time the population difference Δn of the levels in question will be changed principally by means of cross-relaxation with other energy levels. Since the latter are not at that moment in equilibrium with the lattice, the magnitude of Δn at $t = t'$ can be greater than the population difference Δn_{lat} corresponding to the Boltzmann distribution when there is equilibrium between the spin system and the lattice. The population difference will subsequently tend toward Δn_{lat} via the spin-lattice relaxation channel.

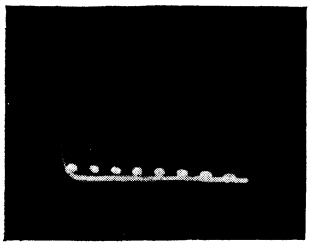

FIG. 2

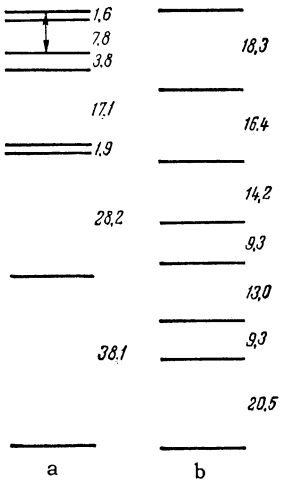

FIG. 3

FIG. 2. Relaxation curve for an absorption line of the "trigonal" Gd^{3+} ions with $\mathbf{H} \parallel [111]$, $T = 1.7°K$, $\mathbf{H} \approx 3360$ Oe, pulse length = 50 msec. The time markers on the base line, which corresponds to Δn_{lat}, are 20 msec in length.

FIG. 3. Energy-level scheme for the "trigonal" Gd^{3+} ions in a field $H \approx 3360$ Oe: a—levels of an ion for which $H \parallel z$; b—levels of unequivalent ions for which $\mathbf{H} \nparallel z$. The energy spacings are given in Gc.

Figure 3 shows the energy-level scheme for the "trigonal" Gd^{3+} ions in the magnetic field corresponding to one of the lines that show a marked cross-relaxation effect. From this diagram it can be seen that there are several energy intervals with closely similar and multiple splittings, and these can lead to effective cross-relaxation effects or, in other words, to a large capacity for the cross-relaxation channel.

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