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SPIN-LATTICE RELAXATION IN CHROMIUM CORUNDUM

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Spin-lattice relaxation of Cr^{3+} ions in corundum single crystals was studied at temperatures of 290, 77 and 4.2°K and at various magnetic dilutions. Continuous saturation of paramagnetic resonance absorption at a frequency of 9375 Mcs was employed. The spin-lattice relaxation times T_1, determined from the saturation of the lines of various electronic transitions, were found to depend on the degree of magnetic dilution. T_1 varies between $10^{-5} - 10^{-6}$ sec for $T = 77°K$ and between $10^{-2} - 10^{-5}$ sec for $T = 4.2°K$ when the Cr^{3+} ion concentration increases with respect to that of the Al^{3+} ions from $\sim 5 \times 10^{-4}$ to 6×10^{-3}. For a sample with a large magnetic dilution, the magnitude of T_1 at $T = 4.2°K$ depends on the saturating power, increasing with increase of the latter. The anomalous character of spin-lattice relaxation in chromium corundum is probably connected with energy transfer processes from the spin system to the thermostat (liquid helium) such as spin-phonon interaction, including phonon diffusion processes and transfer of energy from the lattice to the thermostat.

1. INTRODUCTION

INTEREST in the study of relaxation processes in paramagnets has recently developed in connection with the development of masers. Relaxation phenomena are also of great physical interest in themselves.

The theory of spin-lattice relaxation developed earlier by Kronig and van Vleck was in the main confirmed by the experiments on non-resonance paramagnetic absorption by Gorter and his collaborators, and also by some experiments on the saturation of paramagnetic resonance absorption (see, for example, references 1 and 2 and the bibliography contained in them). Recently "anomalous" spin-lattice relaxation effects have been observed in some paramagnetic crystals at very low temperatures (< 4°K).[1,2] It appeared that the spin-lattice relaxation time could not be explained on the basis of the Kronig-van Vleck theory. In particular, the theory does not explain the temperature and concentration dependence of the relaxation time.

To explain the observed anomalies, Gorter, Townes, Strandberg, Anderson* and others[1-3] put forward various hypotheses based on the assumption that the mechanism of transfer of the phonon energy to the thermostat (liquid helium) plays an important (sometimes dominant) part at low temperatures. Although some experimental data can be explained qualitatively by this mechanism, we should point out that the whole range of data on relaxation at low temperatures could not be explained on the basis of these hypotheses. At present, no rigorous quantitative theory of spin-lattice relaxation has been developed which describes the anomalous low temperature effects mentioned. For such a theory to be developed it is now very necessary to collect experimental data on spin-lattice relaxation over a wide temperature range, especially at low temperatures.

In the present work we present results of an investigation of spin-lattice relaxation of Cr^{3+} ions in single crystals of corundum (Al_2O_3) by the method of continuous saturation. The measurements were made at a frequency of 9375 Mcs at room temperature, liquid nitrogen and liquid helium temperatures. The effect of saturation of different electronic transitions of the "parallel" Cr^{3+} spectrum (see figure) was studied, i.e., for the external steady magnetic field parallel to the trigonal axis of the crystalline electric field.

2. EXPERIMENTAL METHOD

The single crystal specimens of chromium corundum ($Al_2O_3 \cdot Cr_2O_3$) had chromium concentrations (expressed as the ratio of the number of Cr^{3+} ions to the number of Al^{3+} ions, which formed the diamagnetic diluent) 2.2×10^{-5}, 1.5×10^{-4}, 5.3×10^{-4}, 0.9×10^{-3}, 4×10^{-3}, and 6.5×10^{-3}, and were grown from the melt by the Verneuil

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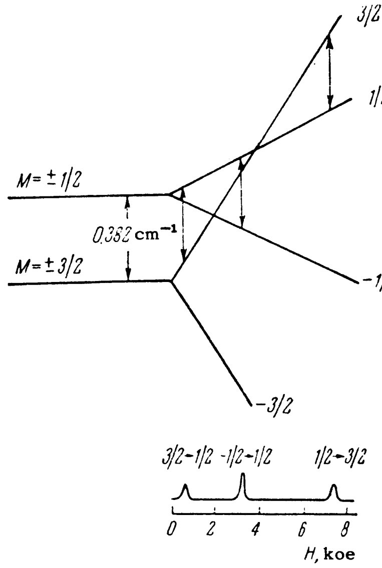
*Paper delivered by P. Anderson at the Physics Institute, Academy of Sciences, U.S.S.R., 1959.



Energy levels and paramagnetic resonance spectrum for Cr^{3+} in corundum, observed at a frequency of 9375 Mcs for parallel orientation of the trigonal axis. The arrows show the electronic transitions corresponding to the spectrum observed.

process. Observation of the effect of saturation in the paramagnetic resonance spectrum of Cr^{3+} was made with a superheterodyne radio-spectrometer, similar to that described by us previously.[4] An automatic tuner and a special resonator with variable coupling are used to observe the resonance lines at low temperatures.[5]

The method of measuring the effect of saturation was the usual one, and consisted of measuring the line intensity of the absorption for various microwave power levels fed to the resonator. As is well known, when saturation occurs, the absorption line intensity is given by the relation

$$J = J_0 / (1 + \beta), \tag{1}$$

where J_0 is the intensity in the absence of saturation and β is the saturation factor equal to $2\gamma^2 H_1^2 T_1 T_2 w$, γ being the gyromagnetic ratio, H_1 the intensity of the microwave magnetic field in the resonator, T_1 the spin-lattice relaxation time, T_2 the spin-spin relaxation time, and w the square of the matrix element of the spin operator for the corresponding electronic transition. Two methods were used for determining the saturation factor. In the first β was determined from the ratio of the intensities of the Cr^{3+} resonance line for different levels of power fed to the resonator for constant power applied to the mixer of the superheterodyne receiver. In the second method β was determined from the ratio of intensities of the absorption line to an absorption line of a standard, the free radical diphenylpicrilhydrazine (DPPH), a specimen of which was included in the resonator with the substance under investigation. Our measurements showed that the DPPH line is not saturated at microwave power levels for which strong saturation of the Cr^{3+} line in corundum is observed. At T = 4.2°K the DPPH line is noticeably saturated for a power of about 30 mw and a loaded-resonator Q of 12×10^3. The saturation factor for the DPPH line was then 0.5.

The specimens were placed in the resonator in pairs to increase the accuracy of the determination of the relaxation times for different Cr^{3+} concentrations. The symmetry axes of the specimens were inclined at a small angle to one another (about 10°) to prevent coincidence of the absorption lines. The saturation factors were measured on the two specimens for the same power level, and parallel orientations for each was achieved by rotating the magnet, thus avoiding detuning of the resonator, which usually happens when the specimen is rotated inside. We checked the linearity of the radio-spectrometer for all measurements (i.e., the dependence of the amplitude of the output signal to the oscillator on the power absorbed at resonance). Linearity was preserved in all cases, i.e., the absorption signal observed on the oscilloscope was proportional to the magnitude of the absorption coefficient (i.e., the imaginary part of the susceptibility — χ'').

The relaxation time is determined by the relation which follows from (1):

$$T_1 T_2 = 10^{-7} \nu V \beta / 8\gamma^2 w Q P, \tag{2}$$

where ν is the frequency (cps) of the microwave source, V the volume (cc) of the resonator, Q the figure of merit of the loaded resonator, and P the power (w) fed to the resonator.

3. RESULTS AND DISCUSSION

As can be seen from Eq. (2), the spin-lattice relaxation time T_1 can be calculated if T_2 is known. T_2 can be derived from the line width if this is determined by homogeneous spin-spin interactions. However, for small Cr^{3+} concentrations the main contribution to the line width comes from the interaction of Cr^{3+} with Al^{27} nuclei, which leads to an inhomogeneous line broadening. As Portis[6] has shown, a formula different from (1) must be used for T_1, and T_2 must be determined only from the spin-spin width and not from the full line width. However, our investigation showed that the saturation effect in the Cr^{3+} line in corundum followed (1),* i.e., we must assume that the value of T_2 in (1) and (2) is determined

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*This test was made on specimens 3 and 4 (see Table II) at a temperature of 77° K. See below for deviations from equation (1) at T = 4.2° K.

TABLE I. Relaxation time of Cr^{3+} in corundum for a specimen with relative concentration Cr : Al = 5.3×10^{-4}

Transition	$T_1 \times 2.5$, sec			T_2, sec
	T,° K = 293	77	4,2	
$-1/2 \rightarrow +1/2$	$6.1\cdot10^{-6}$	$3.2\cdot10^{-4}$	$1.1\cdot10^{-1}$ *	$7,1\cdot10^{-9}$
$3/2 \rightarrow 1/2$	$8,4\cdot10^{-6}$	$4.5\cdot10^{-4}$	$2,7\cdot10^{-1}$ **	$5.5\cdot10^{-9}$
$1/2 \rightarrow 3/2$	$6.6\cdot10^{-6}$	$3.5\cdot10^{-4}$	—	$5.5\cdot10^{-9}$

*T_1 determined for a saturation factor $\beta = 1$.
**T_1 determined for a saturation factor $\beta = 1.5$.

TABLE II. Relaxation time of Cr^{3+} in corundum for specimens of various chromium concentrations. Electronic transition $-\frac{1}{2} \rightarrow +\frac{1}{2}$

Specimen No.	Relative concentration	$T_1 \times 2.5$, sec			$T_2 \times 10^9$, sec
		T,° K = 293	77	4.2	
1	$2.2\cdot10^{-5}$	$5.3\cdot10^{-6}$	—	—	9.5
2	$1.5\cdot10^{-4}$	$5.0\cdot10^{-6}$	$3.8\cdot10^{-4}$	—	8,4
3	$5.3\cdot10^{-4}$	$6.1\cdot10^{-6}$	$3.2\cdot10^{-4}$	$1.1\cdot10^{-1}$*	7,1
4	$0.9\cdot10^{-3}$	$4.1\cdot10^{-6}$	$2.1\cdot10^{-4}$	$1.6\cdot10^{-2}$	6,0
5	$4\cdot10^{-3}$	—	$6.6\cdot10^{-5}$	$1.5\cdot10^{-3}$	2,9
6	$6.5\cdot10^{-3}$	—	$1.0\cdot10^{-5}$	$1.7\cdot10^{-4}$	1.3

*T_1 determined for a saturation factor $\beta = 1$.

by the full line width. Townes and his co-workers found an analogous situation in the effect of saturation for Cr^{3+} in cyanide.[2] We shall not discuss this effect here, although it is of interest in itself from the point of view of explaining the mechanism of saturation of the paramagnetic resonance line. Using the known line width to determine T_2,* we have in this way applied the experimental data on the saturation factors to determine the relaxation time of Cr^{3+} in corundum. These data are given in Tables I and II.

It can be seen from Table I that the values of T_1 corresponding to all three observed transitions of the "parallel" spectrum are not very different from one another. We should point out that because of the high relative accuracy of the measurements, the small differences in T_1, for different transitions at the same temperature, are outside the limits of error.

The small differences of T_1 for different transitions can be explained by considering the mechanism of saturation and spin-lattice relaxation in a system with many energy levels, as occurs for Cr^{3+} ions (four spin levels, corresponding to the electron spin $S = 3/2$). In experiments on saturation, the equilibrium distribution of the paramagnetic ions among the levels (the Boltzmann distribution) during the saturation of one transition is achieved in the spin-lattice relaxation time T_1, which depends on the probability of relaxation transitions between all the spin energy levels of the given paramagnetic ions. The relaxation can be considered to take place via all levels. For multi-level systems, the relaxation time T_1 derived from experiments on saturation will therefore be an average over the relaxation transitions between all levels. It is then clear that although the probabilities of relaxation transitions between different levels may be very different, the difference between the values of T_1, determined by saturation of the lines of the corresponding transitions, may be small, as occurs for Cr^{3+} in corundum.

It can be seen from Table I that the temperature dependence of T_1 is slight, indicating that even at fairly high temperatures first order processes play an appreciable part in spin-lattice relaxation. The strong dependence of T_1 on Cr^{3+} concentration is unexpected (see Table II) and this dependence is different at different temperatures. The dependence of T_1 on concentration at T = 4.2°K is considerably greater than at T = 77°K. In addition, there is a departure from (1) for the effect of saturation at 4.2°K in specimens with large magnetic dilution. In specimen 3 (Table II)

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*We have used the Lorentz formula for the line to calculate T_2, $T_2 = 1/\pi\Delta\nu$, where $\Delta\nu$ is the half-width in the absence of saturation, although in chromium corundum the lines lie between the Lorentz and Gauss shapes.[7] However, since the values of T_2 for Lorentz and Gauss lines are little different, and the line shape is very little dependent on Cr^{3+} concentration,[7] we have used Eq. (1) for T_2.

the value of β/P does not remain constant as β changes from 0.5 to 5, but increases by more than a factor of two. For the more concentrated specimen 4, the value of β/P does not change as β varies from 0.8 to 4.5.

The experimental results obtained cannot be explained by the usual theory of spin-lattice relaxation. One must suppose that energy transfer processes from the spin system to the thermostat (liquid helium) are important, such as spin-phonon interaction, including phonon diffusion processes and energy transfer from the lattice to the thermostat. These anomalous relaxation processes in corundum are surprising as it has a high thermal conductivity, in contrast to crystals studied earlier in which such anomalous relaxation processes are found.[1,2]

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