ON THE NATURE OF SPIN-LATTICE INTERACTION IN CHROME CORUNDUM. I.

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The temperature dependence of the spin-lattice relaxation time of corundum containing various amounts of chromium has been studied by continuously changing the temperature from 4 to 90° K. At small concentrations, the relaxation is determined by the Kronig-Van Vleck mechanism. At high chromium concentrations a new spin-lattice mechanism arises, which apparently is due to an exchange interaction between pairs of chromium ions. The spin-lattice relaxation of chrome corundum samples irradiated in a reactor has been investigated. The measurements were made at 3.2 cm by the CW saturation technique.

1. INTRODUCTION

CHROME corundum (ruby) is now widely used as the working substance in paramagnetic amplifiers. Spin-lattice relaxation plays a very important role in the operation of these amplifiers. Hence a considerable number of experimental papers have been devoted to the study of spin-lattice relaxation in chrome corundum.[1-5]

It has been established,[2] that at liquid-helium temperatures the spin-lattice relaxation time τ_1, measured by the CW saturation method, depends strongly on the concentration of paramagnetic ions, e.g., for a sample with a chromium concentration $c = 5 \times 10^{-4}$ the magnitude of τ_1 is 4.4×10^{-2} sec, and for a concentration of 4×10^{-3}, $\tau_1 = 6 \times 10^{-4}$ sec. (Concentration is defined as the ratio of the number of Cr^{3+} ions to the number of Al^{3+} ions in the corundum lattice.) At liquid-nitrogen temperatures the dependence of the relaxation time on concentration is weaker[2,5]: for the same samples τ_1 is respectively 1.3×10^{-4} and 2.7×10^{-5} sec. The Kronig[6] and Van Vleck[7] classical theory of spin-lattice relaxation, which was developed for isolated paramagnetic ions in a crystal lattice, does not contain a dependence on the concentration of the paramagnetic ions.

Experiments by the pulse method have shown that the spin-lattice relaxation process at low temperatures is complicated by cross relaxation effects.[8,9] Cross relaxation has explained a number of anomalies in the relaxation phenomena at low temperatures (cross saturation, the presence of "fast" exponents in the process of recovery of the intensity of saturated lines, etc.) However, cross relaxation cannot explain the concentration dependence of τ_1; while it equalizes the spin temperature of different transitions, it cannot change the rate of energy interchange between the spin system and the lattice.

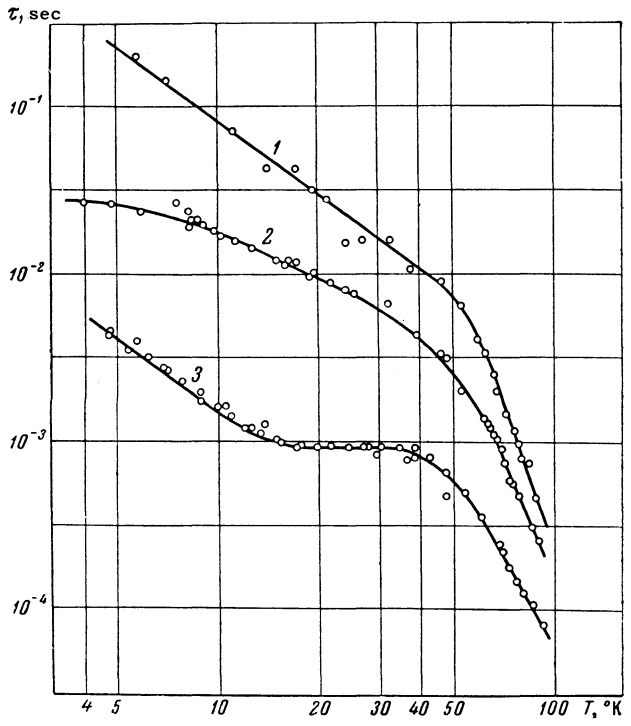
A single relaxation mechanism is insufficient to explain all of the experimental data at low temperatures. It is natural to suppose that several mechanisms take part simultaneously in the spin-lattice relaxation process, each one predominating at a different temperature.

The goal of our investigation of spin-lattice relaxation in chrome corundum was the elucidation of the nature of these mechanisms. All the measurements were made at a frequency of 9400 Mc by the CW saturation method.

2. INVESTIGATION OF SPIN-LATTICE RELAXATION IN IRRADIATED CHROME CORUNDUM.

Van Vleck pointed out as early as 1941, that at low temperatures a limit to the rate of spin-lattice relaxation could exist because of the lack of low-frequency oscillators for the transfer of the energy to the walls of the sample.[10] This idea has been extensively discussed more recently by Gorter, van der Marel, and Bölger,[11] by Townes and his co-workers,[12] and by others.

The limitation due to the lack of low-frequency phonons is withdrawn if there exist processes that widen the frequency band of oscillators interacting with the spins. The scattering of phonons by cracks and lattice defects can serve as such processes. We have made a comparison of the spin-lattice relaxation times of samples having the same concentration of chromium, but a different concentration of defects.



The lattice defects (principally in the form of atoms displaced from their equilibrium positions) were created by irradiation with fast neutrons and gamma rays in the active zone of a reactor. The number of defects in the irradiated samples was of the order of 10^{19} cm^{-3}.[13] After irradiation, the electron paramagnetic resonance spectrum in parallel orientation ($\theta = 0°$) was measured. The line positions had not changed, but transitions between the levels with quantum numbers $+\frac{3}{2}$ and $+\frac{1}{2}$ were significantly widened: the width had increased from 15 to 70 oe. The line corresponding to the transition $+\frac{1}{2} \longleftrightarrow -\frac{1}{2}$ was unchanged.*

The spin-lattice relaxation time τ_1 of the transition $+\frac{1}{2} \longleftrightarrow -\frac{1}{2}$ in the parallel orientation, for the irradiated sample with chromium concentration of 2×10^{-4}, turned out to be three times shorter than τ_1 for the non-irradiated control sample of the same concentration. For samples of concentration 8×10^{-4} the relaxation time τ_1 of the irradiated sample was only 1.3 times shorter than τ_1 for the corresponding control sample.

These experiments were conducted at T = 4.2°K. At 77° K the relaxation times of the irradiated samples were the same as those of the control samples. It is to be noted that the number of low-frequency phonons in the control sample should not increase significantly with an increase in chromium concentration, since the scattering from isomorphous paramagnetic centers in the crystal is not significant, and the number of defects in the lattice of the non-irradiated samples is not large (no line broadening due to lattice non-ideality was observed in the samples of both concentrations studied).

Thus, phonon effects play a role only in samples with a low chromium content.* At higher concentrations new relaxation mechanisms appear, not limited by a lack of low-frequency oscillators.

3. INVESTIGATION OF THE TEMPERATURE DEPENDENCE OF τ_1 IN THE RANGE 4 — 90° K.

The different mechanisms of spin-lattice relaxation should show up differently at different temperatures. The results of Manenkov and Prokhorov[2] show that the sharp dependence of τ_1 on concentration at helium temperatures is replaced at T = 77° K by a weaker dependence. At room temperature τ_1 is practically identical for all concentrations. It would be extremely interesting to follow the course of the temperature dependence of τ_1 for different concentrations by continuously changing the temperature. To this end a special apparatus was constructed, with the cavity enclosed by a liquid-helium cooled jacket.[15] By heating the cavity it was possible to obtain any temperature between 2 and 60° K for a prolonged length of time. The temperature was monitored with a carbon thermometer. Use of liquid nitrogen as a coolant makes the higher temperature region 60 — 100° K available for study.

The line width of chrome corundum does not depend on temperature. We used a cavity whose loaded Q likewise did not change with temperature. Hence it was possible to study the dependence of τ_1 on T by measuring the power necessary to saturate a given transition at different temperatures. The results of these measurements for three different chromium concentrations are shown in the

*The noticeable widening of the transitions $+\frac{3}{2} \leftrightarrow +\frac{1}{2}$ is due to the following circumstance. The energy of these transitions ($h\nu = \pm 2D \mp g_{\parallel} \beta H$) depends on the values of the spin Hamiltonian parameters D and $g_{\parallel}$. The disturbance to the regularity of the crystallographic surroundings causes the electric field at the location of a chromium ion to change slightly from ion to ion. This change leads to a variation in the values of the spin Hamiltonian parameters such that the variation in D is very much greater than the variation in $g_{\parallel}$. The theory[14] gives the following relation between the parameters: $2D = \lambda(g_{\parallel} - g_{\perp})$. Since the g-factors are close to one another, the dispersion of the values of D exceeds by three orders the dispersion of the g-factors.

*Attempts to detect a dependence of spin-lattice relaxation time on size (for the concentration of 2×10^{-4}) were unsuccessful; τ_1 was the same within 10% for samples, the smallest linear dimensions of which differed by a factor of four.

figure. The relaxation time studied was that of the transition $+\frac{1}{2} \longleftrightarrow -\frac{1}{2}$. The angle θ was chosen equal to 5°, in order to avoid the possibility of cross relaxation with the transition $-\frac{1}{2} \longleftrightarrow +\frac{3}{2}$.

Curve 1 shows the temperature dependence of the spin-lattice relaxation time for a sample having a chromium concentration $c = 2 \times 10^{-4}$. At temperatures below 50° K, $\tau_1 \sim T^{-1.5}$, and in the interval 64 — 90° K, $\tau_1 \sim T^{-7}$. Curve 2 is for a sample with $c = 8 \times 10^{-4}$. In this case, $\tau_1 \sim T^{-5}$ in the 64 — 90° K interval; it is impossible to characterize the temperature region below 50° K by a single power law. Curve 3 corresponds to a concentration of 2.8×10^{-3}. In the interval 4.2 — 12° K, $\tau_1 \sim T^{-1.3}$; at temperatures from 15 — 32° K, the relaxation time is practically constant, and in the 64 — 90° K range, the magnitude of $\tau_1 \sim T^{-4}$. The precision of the relative measurements of τ_1 is ±10%.

4. DISCUSSION OF THE RESULTS

The curves of τ_1 as a function of temperature for the three chromium concentrations are essentially different in character.

Curve 1, which pertains to the most dilute sample, corresponds approximately to the Kronig-Van Vleck mechanism. Up to 50° K, the relaxation is basically due to the direct process of absorption and emission of single phonons. At higher temperatures processes of Raman scattering of phonons prevail; hence in this range τ_1 strongly depends on temperature ($\tau_1 \sim T^{-7}$).

With an increase in paramagnetic-ion concentration, a new mechanism enters into the relaxation process. It appears particularly pronounced in curve 3, corresponding to the sample with chromium concentration 2.8×10^{-3}. This mechanism shortens the spin-lattice relaxation time at helium temperatures. In the temperature interval 4 — 32° K the relaxation is completely determined by this mechanism; at higher temperatures the Kronig-Van Vleck mechanism also takes part. It is likely that the mechanism that determines the concentration dependence of τ_1 at helium temperatures is relaxation through the exchange interaction of pairs of chromium ions.

The optical investigations of Shawlow, Wood, and Clogston[16] have shown that the fluorescence spectrum of ruby has certain lines which cannot be attributed to transitions between levels of individual Cr^{3+} ions: at a chromium concentration of 3×10^{-4} these lines are absent, and at higher concentrations their intensity increases approximately as the square of the concentration.

The weak lines appearing in the vicinity of the electron paramagnetic resonance lines that belong to transitions between levels of individual Cr^{3+} ions are also associated with exchange interactions of ion pairs.[17]

It can be considered that exchange interaction is also responsible for the anomalies in the relaxation process at low temperatures. At very low paramagnetic-ion concentration, when the number of exchange pairs is small, spin-lattice relaxation is determined by the Kronig-Van Vleck mechanism. This is confirmed by the fact that at extremely low concentrations there is no dependence on concentration. With an increase in concentration the contribution of the exchange relaxation mechanism becomes important. At concentrations of 5×10^{-4} — 5×10^{-3} this mechanism will come in strongly at helium temperature. At still higher concentrations this mechanism will show up even at nitrogen temperatures.

Curve 3 of the figure shows how the probability of exchange relaxation changes with changing temperature. At temperatures of 4.2 — 12° K, τ_1 is approximately proportional to T^{-1}. With further increase in temperature, τ_1 is independent of temperature. The temperature dependence of τ_1 in the interval 32 — 90° K reflects the simultaneous participation of a mechanism giving a T^{-7} dependence and one independent of temperature.

In order to explain the existence of the "plateau" in curve 3 of the figure, we have to suppose that there is an exchange heat reservoir, as postulated by Bloembergen and Wang.[18] In this model the energy of the spin system is first transferred to the exchange reservoir, and from there falls directly into the lattice. At very low temperatures the rate of transfer of energy from the spin system is determined by the transfer process out of the exchange reservoir into the lattice, which depends on temperature. At higher temperatures the probability of a relaxation transition is determined by the process of energy transfer from the system into the exchange reservoir, which does not depend on temperature.

The process of spin-lattice relaxation by means of exchange of ion pairs includes the process of transfer of excitation from the spins of single Cr ions to spins of associated pairs. This transfer undoubtedly occurs through cross spin relaxation and can include spin diffusion processes.

Note that the "plateau" in the curve cannot be successfully explained by a single cross-relaxation process, if this curve is obtained by the CW method. Cross relaxation changes only the effective width of the saturated line.

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