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RELAXATION PHENOMENA IN THE PARAMAGNETIC RESONANCE OF Mn^{2+} *IONS IN THE CUBIC CRYSTAL FIELD OF* SrS

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Relaxation phenomena in the electron paramagnetic resonance spectrum of Mn^{2+} ions in the SrS lattice were studied at a frequency of 9,300 Mc/sec in polycrystalline specimens containing ~ 0.05% Mn. The spin-lattice relaxation time T_1 is 5×10^{-8} sec at 300°K, 1.5×10^{-6} sec at 77°K, 9×10^{-2} sec at 4.2°K and 2.1×10^{-1} sec at 1.6°K. The spin-spin relaxation time T_2, determined from the line width at 77°K, is 6×10^{-8} sec.

Pronounced spin-spin cross relaxation effects were observed at liquid helium temperatures. The spin-spin cross relaxation times in the Mn^{2+} spectrum lie between 2×10^{-3} and 1×10^{-2} sec. The features of spin-lattice relaxation of ions in the S state are discussed. It is indicated that spin-lattice interaction may play an effective role via the covalent bond between the Mn^{2+} ions and the surrounding crystal ions.

1. INTRODUCTION

IN the existing theory of spin-lattice relaxation in paramagnetic crystals it is assumed that the Kronig mechanism is the most effective in the exchange of the electron spin energy of the paramagnetic ions with the thermal vibrations of the lattice. This consists in the modulation of the crystal electric field by the thermal vibrations of the lattice, which is transmitted to the electron spins by means of the spin-orbit coupling.

The case of ions in an S state (Mn^{2+}, Fe^{3+}, Gd^{3+}, Eu^{2+}) in a cubic crystal field is of special interest in connection with the efficiency of this mechanism. In so far as the orbital momentum of such ions is zero in the ground state, there is no spin-orbit coupling, so that the Kronig mechanism should be little effective. This mechanism can only occur for ions in an S state if there is admixture of higher orbital states, with non-zero orbital momentum, to the ground state.

In the present work we have undertaken a study of the spin-lattice relaxation of Mn^{2+} ions in SrS crystals. As was shown by a study of the paramagnetic resonance spectrum of Mn^{2+} in SrS,[1] the crystal field has cubic symmetry and the ^6S ground state is very weakly split (splitting $\sim 10^{-4}\ cm^{-1}$). This indicates that the ground state of Mn^{2+} in the SrS cubic lattice is almost a pure S state, and it would, therefore, be expected that the spin-lattice relaxation time should be large even at room temperature. However, it turned out that the spin-lattice relaxation time of Mn^{2+} in SrS is fairly short ($\sim 10^{-8}$ sec at room temperature and $\sim 10^{-6}$ sec at liquid-nitrogen temperature). We discuss below these results on the basis of possible relaxation mechanisms.

Apart from features connected with spin-lattice relaxation, the case of Mn^{2+} ions is also of interest from the point of view of the elucidation of the role of spin-spin cross relaxation, since Mn^{2+} ions have a large number of hyperfine structure energy levels, brought about by the interaction of the electron spin of Mn^{2+} ($S = 5/2$) with the nuclear spin of Mn^{55} ($I = 5/2$). The phenomenon of cross relaxation was analyzed in detail theoretically by Bloembergen et al[2] and was found experimentally and studied in various substances by several authors (see, for example,[3,4]).* We have observed very pronounced cross relaxation effects in the spectrum of Mn^{2+} in SrS at liquid-helium temperatures.

2. EXPERIMENTAL METHODS OF STUDYING RELAXATION PROCESSES

The investigation of relaxation was carried out on SrS·Mn single crystal specimens with a Mn^{2+} ion concentration of about 0.05%.

The measurements of relaxation time were made with a superheterodyne radiospectrometer at a frequency of 9,300 Mc/sec at room temperature

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*The cross relaxation effects observed by Giordmaine et al[3] were explained by Bloembergen et al[2] as spin-spin cross relaxation phenomena.

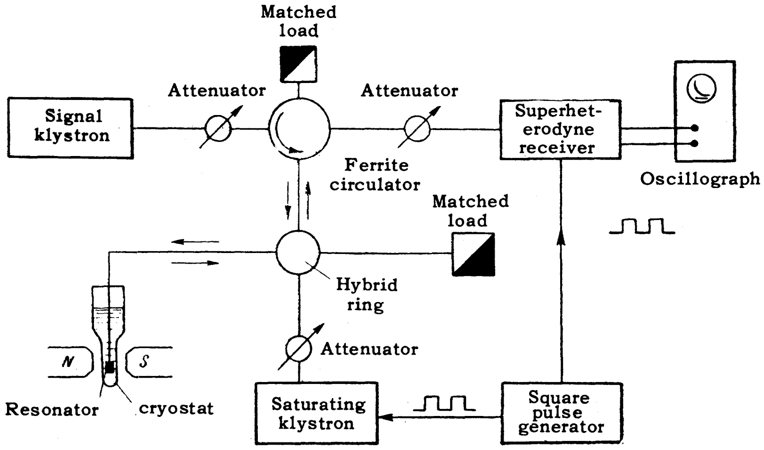

FIG. 1. Block diagram of apparatus used in the relaxation studies.

(300° K), liquid-nitrogen (77° K) and liquid-helium temperatures (4.2° and 1.6° K).

All the measurements were carried out for different hyperfine structure components, $m = \pm 1/2$; $\pm 3/2$; $\pm 5/2$ on the lines corresponding to the electronic transition $M = 1/2 \rightarrow -1/2$. At 300° K the spin-lattice relaxation time T_1 was calculated from the line broadening produced by spin-lattice interaction. This broadening was determined by a comparison of the line widths at 300 and at 77° K.

The value of T_1 at 77° K was determined by the method of continuous saturation of the lines. The method of measurement is analogous to that described earlier.[8]

The relaxation phenomena at liquid helium temperatures were mainly studied by the method of pulsed saturation of the lines of the spectrum. The block diagram of the apparatus used in these experiments is shown in Fig. 1. Saturation was produced by square pulses from an auxiliary klystron generator, the frequency of which was made equal to the frequency of the signal klystron.

The heterodyne only works in the intervals between the saturating pulses, in order to avoid saturation of the heterodyne receiver by the strong signal from the auxiliary klystron. The pulse mode of operation of the saturating klystron and of the heterodyne klystron is produced by feeding the voltages from the square pulse generator onto the reflector.

The observation of the relaxation curves of the recovery of the intensity of the absorption lines in the periods between the saturating pulses is carried out for low power levels of the signal klystron, working under continuous wave conditions.

The duration of the saturating pulses τ was varied in two series of experiments. Saturation by narrow ($\tau = 0.1 - 1$ μsec) and by wide ($\tau = 70$ μsec) pulses was carried out in order to separate the effects of spin-spin cross relaxation and of spin-lattice relaxation (for further details, see Sec. 3).

At 4.2° K the relaxation times were also determined by continuous saturation, in order to compare the values obtained by this method with the values of relaxation time determined by the pulsed saturation method.

3. EXPERIMENTAL RESULTS

The spin-lattice relaxation time T_1 for Mn^{2+} ions in SrS at room temperature was determined from the line broadening, produced by spin-lattice interaction, of the electronic transition $M = 1/2 \rightarrow -1/2$ for the two hyperfine structure components corresponding to values of the nuclear magnetic quantum number $m = \pm 5/2$.* The $M = 1/2 \rightarrow -1/2$ lines are best resolved for these components. For both lines the value of T_1 is the same, equal to $T_1 = 5 \times 10^{-8}$ sec. At 77° K, T_1 was determined by the continuous line saturation method. As is well known, the product $T_1 \cdot T_2$ is determined directly by this method. We obtained the value 9.2×10^{-14} sec^2 for this product at 77° K, and this was the same for the two lines studied, $M = 1/2 \rightarrow -1/2$, $m = \pm 5/2$. The spin-spin relaxation time T_2 calculated from the observed width $\Delta\nu$ of these lines at $T = 77°$ K, using the relation $T_2 = 1/\pi\Delta\nu$, is 6×10^{-8} sec and the spin-lattice relaxation time is consequently $T_1 = 1.5 \times 10^{-6}$ sec.

At liquid helium temperature, $T = 4.2°$ K, the continuous saturation method for the transition $M = 1/2 \rightarrow -1/2$, $m = \pm 5/2$ gave the value $T_1 = 2.9 \times 10^{-2}$ sec, if the same value of T_2 is used as at $T = 77°$ K. However, in the presence of spin-spin

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*Detailed data on the spectrum of Mn^{2+} in SrS at 300 and at 77°K were obtained earlier.[1] The spectrum observed at liquid helium temperatures was little different from the spectrum at 77°K.

cross relaxation, which is strongly marked in the spectrum of Mn^{2+} in SrS at helium temperatures, the effective value of T_2 must be reduced threefold in order that the value of T_1 should agree with the true value of the spin-lattice relaxation time $T_1 = 9 \times 10^{-2}$ sec, determined by the direct method of pulsed saturation (see below). For a more detailed investigation of relaxation processes in the paramagnetic resonance spectrum of Mn^{2+} in SrS at helium temperatures, we applied the method of pulsed saturation of the lines.

On saturating by narrow pulses of duration $\tau = 0.1 - 1$ μsec, it was immediately noticed that the relaxation curve of the recovery of the absorption line intensity J, after the action of the saturating pulses, consists of several exponentials and can be expressed by the formula

$$J = \sum_i [A_i \exp(-\alpha_i t) + B_i],$$

where A_i, α_i, and B_i are constants independent of the time t.

Figure 2 shows an oscillogram of a typical relaxation curve, obtained for a saturating pulse duration $\tau = 1$ μsec, for the line of the transition $M = 1/2 \rightarrow -1/2$, $m = -1/2$ at $T = 4.2°K$. The base line below the relaxation curve corresponds to the equilibrium intensity of the line in the absence of saturation $J_0 = \sum_i B_i$. It was established that the coefficients α_i of the rapidly falling exponential are independent of temperature in the range 4.2 — 1.6° K for all the transitions studied $M = 1/2 \rightarrow -1/2$, $m = \pm 1/2; \pm 3/2; \pm 5/2$, while $T_i = 1/\alpha_i$ has values within the limits 2 — 10 μsec. For all the transitions $M = 1/2 \rightarrow -1/2$, $m = \pm 1/2; \pm 3/2; \pm 5/2$ there is a slowly falling exponential in the overall relaxation curve, the exponent of which decreases with decreasing temperature. The weighting factor of this exponential for all the transitions studied is on the average ~ 50% of the equilibrium line intensity ($A/J_0 \sim 0.5$). The values of $1/\alpha_i$ for the slowly falling exponentials varied between 23 — 46 μsec at 4.2° K and 150 — 200 μsec at 1.6° K for the transitions $M = 1/2 \rightarrow -1/2$, corresponding to different components of the hyperfine structure (to different values of m).

The fact that the relaxation times $T_i = 1/\alpha_i$ for the rapidly falling exponentials are independent of temperature, shows that these exponentials characterize the spin-spin interaction. The slowly falling exponentials evidently characterize the spin-lattice interaction, since the relaxation times corresponding to them depend on temperature.

We carried out an experiment with saturation of the lines by broad pulses of duration $\tau = 70$ μsec in order to elucidate the nature of these two processes. During the time of action of the saturating pulse, the duration of which is greater than the spin-spin cross relaxation time, the saturation processes within the spin system have time to get established, and after the removal of the saturating pulse only spin-lattice relaxation should be observed.

FIG. 2. Oscillogram of relaxation curve for the transition $M = 1/2 \rightarrow -1/2$, $m = -1/2$ at $T = 4.2°K$. Saturating pulse duration $\tau = 1$ μsec, pulse repeat time $\tau_1 = 50$ μsec.

It turned out in fact that on saturating by a broad pulse, the relaxation curve was in the form of only one slowly falling exponential. Thus the relaxation time corresponding to this exponential is the spin-lattice relaxation time T_1. The time T_1 is the same for all transitions

$$M = 1/2 \rightarrow -1/2, \quad m = \pm 1/2; \quad \pm 3/2; \quad \pm 5/2$$

and has the value $T_1 = 90$ μsec at 4.2° K and $T_1 = 210$ μsec at 1.6° K. The values $1/\alpha_i$ for the slowly falling exponentials, obtained on saturating by narrow pulses, are less than the values of T_1. This fact shows that the long exponentials on saturating with narrow pulses characterize a mixture of spin-lattice and spin-spin cross relaxation processes. After carrying out the experiments on saturation by broad pulses it becomes more certain that the times $T_i = 2 - 10$ μsec for the rapidly falling exponentials, observed in the experiments on saturation by narrow pulses, refer to spin-spin cross relaxation.*

4. DISCUSSION OF RESULTS

The following conclusions about the character of the relaxation processes in the spectrum of Mn^{2+} in SrS can be drawn from the experimental results.

1. The temperature dependence of the spin-lattice relaxation time follows the law $T_1 \sim T^{-1}$ in the range 4.2 — 1.6° K. This shows that single phonon processes are dominant in spin-lattice relaxation at helium temperatures. At higher temperatures the $T_1 = f(T)$ dependence becomes steeper. It is interesting to note that the reduction of T_1 on increasing the temperature from 4.2 to

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*Analogous phenomena of cross relaxation were observed in the spectrum of Co^{2+} in Al_2O_3.[6]

300° K appears not to proceed monotonically. This deduction follows from the fact that the temperature dependence follows a law $T_1 \sim T^{-n}$, where the power n, using the values of T_1 determined at 300, 77 and 4.2° K, comes out larger in the range 4.2 — 77° K than in the range 77 — 300° K. We may also note that at 300° K, $T_1 \approx T_2$ within the limits of experimental errors. Investigations of spin-lattice relaxation at other points in the range are essential for drawing more reliable conclusions about the temperature dependence of T_1 in the range 300 — 4.2° K.

2. The Mn^{2+} ions are in an S-state and the crystal field splits the energy levels of Mn^{2+} in SrS little. We could therefore have assumed that the Kronig mechanism would be little effective for spin-lattice relaxation of Mn^{2+} in SrS, and expect a reasonably large relaxation time T_1 even at room temperature. However, the values of T_1 turned out to be unexpectedly small at 300 and at 77° K. Although the Kronig mechanism can make a contribution to spin-lattice relaxation through the admixture of higher orbital states, it is possible that other relaxation mechanisms play a part in the case of Mn^{2+} in SrS.

Al'tshuler[9] discusses theoretically two mechanisms which may be important for the relaxation of ions in an S-state: modulation, by the thermal vibrations of the lattice, of the magnetic (the Waller mechanism) and exchange interactions between paramagnetic ions. Detailed calculations are necessary to estimate the contribution of these mechanisms to the spin-lattice relaxation of Mn^{2+} in SrS, although it appears unlikely that it can be large, in so far as the concentration of Mn^{2+} ions in the specimens studied is small (~ 0.05%).

Apart from the relaxation mechanisms noted above, we assume that for Mn^{2+} in SrS, spin-lattice relaxation can be brought about by the modulation of the covalent bonding of Mn^{2+} with the surrounding diamagnetic ions. This mechanism has not so far been discussed theoretically, but it may be effective in substances with covalent bonding. The reduction in the hyperfine structure constant for Mn^{2+} in this compound[1] indicates the existence of covalent bonding of Mn^{2+} in SrS with the surroundings.

3. Spin-spin cross relaxation is strongly marked in the relaxation processes of Mn^{2+} in SrS at liquid helium temperatures.

This cross relaxation may be brought about in the spin system by transitions between energy levels of the electron spin of Mn^{2+}, corresponding to different electron and nuclear states (different values of the electronic, M, and nuclear, m, magnetic quantum numbers). In other words, cross relaxation in the paramagnetic resonance spectrum of Mn^{2+} may proceed between different components of the hyperfine structure, corresponding to one and the same electronic transition, and also between lines belonging to different electronic transitions within each component of the hyperfine structure. Mn^{2+} ions have a large number of energy levels, equal to $(2S + 1)(2I + 1) = 36$, and a complicated paramagnetic resonance spectrum consisting of six groups of hyperfine structure lines, with splittings in these groups into several lines belonging to different electronic transitions. It is therefore difficult to give a definite interpretation of the cross relaxation times observed by us in experiments with pulsed saturation of absorption lines, since there are a large number of routes by which cross relaxation processes may proceed.

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