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Measurement of electron spin-spin relaxation by an optical labeling technique

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The electron spin-spin relaxation due to flip-flop of like spins, which cannot be detected by magnetic methods, was measured by optical means for the first time in ruby (0.05 wt.%). Irradiation with a narrow-band laser produces an internal nonequilibrium in the ground-state spin system ($S_z = \pm\frac{1}{2}$ levels in $^4A_2$) and recovery from the nonequilibrium by spin-spin relaxation is measured by monitoring the time evolution of the optical holes. The observed spin-spin relaxation time (~ 0.5 ms) was much longer than the transverse decay time estimated from electron spin-echo decay. The spin-spin relaxation in dilute ruby (0.0034 wt.%) was too slow to be observed.

It is known that the thermal equilibrium of a spin system in a paramagnetic solid is achieved by spin-lattice relaxation (SLR) and spin-spin relaxation (SSR). If the SLR time is much longer than the SSR time, an internal equilibrium described by a spin temperature is established by SSR before SLR is completed.[1] In this context we use the term SSR for the establishment of the internal equilibrium. The SSR is generally different from the transverse relaxation (TR) which represents the decay of coherence. Although the TR time is sometimes regarded as a characteristic time for the establishment of the internal equilibrium, this is not always true. Generally SSR time is longer than the TR time.

In this Rapid Communication we deal with the establishment of the internal equilibrium of a spin system consisting of like spins with fictitious spin $\frac{1}{2}$ in high magnetic fields where the level spacings are much larger than the spin-spin interactions. In this case flip flops of the spins are responsible for the SSR. To our knowledge, the SSR due to flip flop of like spins has not been measured so far, in spite of its importance in spin thermodynamics. This Rapid Communication reports the first measurement of the SSR time in an electron paramagnetic solid (ruby).

The TR time (spin-echo decay time) of ruby (0.005 wt.%) in a high magnetic field (~ 3 kOe) is of the order of μs.[2] The TR time of our sample (0.05 wt.%) in a lower field (0.35 kOe) should be less than μs because the TR time diminishes as the concentration increases and/or the field diminishes. We found that the SSR time is much longer than ($\gtrsim 10^3$ times) the TR time.

The SSR time measured here may be called intraline cross relaxation[3] time.

Magnetic methods which detect total magnetization cannot detect the SSR. The measurement of the SSR time was made by using an optical method as follows. The essence of the method is in the optical labeling of magnetically indistinguishable spins. The lower two levels ($\pm\frac{1}{2}$)$^4A_2$ in Fig. 1 are magnetic sublevels of the ground state for which SSR is to be measured. Hereafter we abbreviate $(+\frac{1}{2})^4A_2$ and $(-\frac{1}{2})^4A_2$ as $|+\rangle$ and $|-\rangle$, respectively. The upper two levels are sublevels of the optically excited state $\bar{E}(^2E)$ and are represented by sloped lines to show schematically the presence of an inhomogeneous distribution of optical-transition frequencies. Two optical transitions $\sigma_-[|+\rangle \leftrightarrow (+\frac{1}{2})\bar{E}(^2E)]$ and $\sigma_+[|-\rangle \leftrightarrow (-\frac{1}{2})\bar{E}(^2E)]$ are allowed for σ light. The sample is first irradiated with a narrow-band laser (σ polarized) tuned to the R_1 line. A small number of ions ("labeled ions") are brought into resonance and a narrow-optical hole (center hole) is burned in the inhomogeneously broadened R_1 line resulting in the decrease of the population in one of the ground-state sublevels $|+\rangle$. This causes internal nonequilibrium in the ground-state spin system. The duration of irradiation is assumed to be shorter than the SSR time. The equilibrium is restored by the SSR [Fig. 1(b)]. Since the spins (labeled spins) associated with the labeled ions are only a small fraction of the total spins, the SSR occurs mainly through the flip flop of labeled and unlabeled spins. The SLR time in $^4A_2$ and the radiative decay time are much longer than the SSR time in the present case. The decrease of the population in the other ground-state sublevel $|-\rangle$ of the labeled ions caused by the SSR gives rise to another hole (side hole)[4] at the shifted frequency [Fig. 1(c)]. Measurement of the decay of the center hole or the growth of the side hole

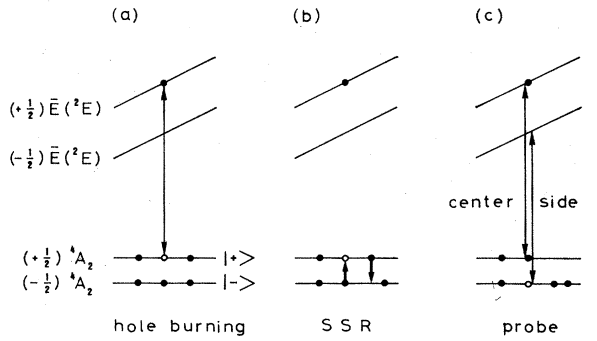

FIG. 1. Relevant energy levels and the illustration of the method. (a) Irradiation with a laser creates a narrow optical hole (center hole) for the σ transition. (b) The equilibrium in the ground-state spin system is restored by the spin-spin relaxation. (c) The SSR is detected by monitoring the decay of the center hole and the growth of the side hole.

due to the time evolution of the population distribution of the labeled spins gives the SSR time. Strictly speaking the spin system for which the SSR is measured is different from the original one because some of the spins in the ground state are replaced by those in the optically excited state. However, as long as the number of the replaced spins is small, the difference is considered to be negligible.

There are two types of labeled ions (I) and (II), whose σ_- and σ_+ transitions, respectively, are resonant with the laser. Figure 1 shows the behavior of the ions (I). The contribution of the ions (II) is quite similar. The labeled spins are considered to be randomly distributed in space. It is worthwhile to note that the inhomogeneous broadening of electron spin resonance (ESR) between levels $|+\rangle$ and $|-\rangle$ is much smaller than that of optical-transition frequencies and no correlation exists between them.[5] Therefore the optical pumping creates a nonequilibrium state where the ground-state spins are depleted uniformly over the inhomogeneous distribution associated with the ESR. This state is quite different from that created by ESR hole burning.

The experimental setup is similar to that in a previous experiment.[6] The creation and the observation of the holes are achieved by using a Stark switching technique[7] under the irradiation with a cw ruby laser pumped by an Ar ion laser. A static magnetic field $H=350$ Oe and a Stark field are applied parallel to the c axis of the sample ruby (0.05 wt.%) cooled at ~ 2 K. During the first rectangular Stark pulse (50 V, 50 μs) in Fig. 2(a) the center hole is burned. After a time interval T the transmitted light intensity is monitored by applying a second rectangular pulse with voltage V. The time interval T is longer than the optical-dephasing time. The change in the absorption due to the first pulse is shown in Fig. 3. The center and side holes are observed at $V=50$ and 210 V, respectively. The side hole is separated from the center hole by 226 MHz (160 V) which is the difference between the optical-transition frequencies of σ_+ and σ_- at $H=350$ Oe. When T is short ($T=100$ μs) only the center hole is observed [Fig. 3(a)]. As T is increased ($T=1.2$ ms) the side hole becomes apparent as a result of SSR [Fig. 3(b)]. The sum of the areas of the center and side holes was found to be almost constant when $T<2$ ms. This indicates that the SSR occurs mainly between $|+\rangle$ and $|-\rangle$.

The time evolutions of the center and side holes were observed separately by using the pulse sequence shown in Fig. 2(b). When the height of the first pulse is 50 V (or 210 V), the center (or side) hole is observed. Here different labeled spins are used for the observations of the center and side holes. The observed hole heights versus T are plotted in Figs. 4(a) and (b). It was observed that the width of the holes was nearly constant. The decay time of the center

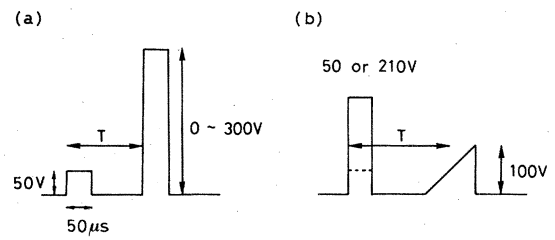

FIG. 2. Two types of Stark pulse sequences (a) and (b) used for the detection of SSR.

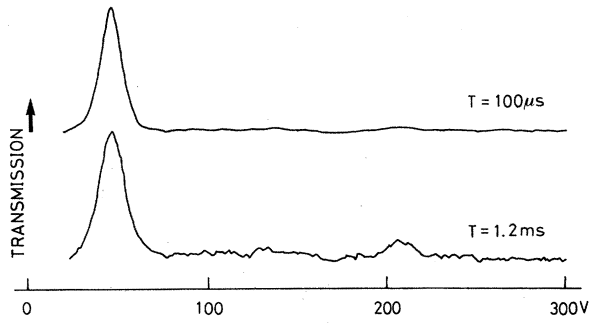

FIG. 3. The center and side holes detected at $V=50$ and 210 V by using the pulse sequence in Fig. 2(a). Only the center hole is detected for short T. As T is increased ($T=1.2$ ms) the side hole appears by SSR. The heights of the center holes are set to be unity.

hole which is due to SSR is shorter than the SLR time (~ 0.5 s) (Ref. 8) in $^4A_2$ and the radiative lifetime (4.3 ms).[9]

We performed a calculation based on the rate equations.[10] A fit to the experiment is obtained by using SSR times of 0.5 ms for $|+\rangle \leftrightarrow |-\rangle$ and 3 ms for $|\pm\rangle \leftrightarrow (\pm\frac{3}{2})^4A_2$ and the SLR time in $\bar{E}(^2E)$ of 30 ms. The longer SSR time (3 ms) for $|\pm\rangle \leftrightarrow (\pm\frac{3}{2})^4A_2$ compared with that (0.5 ms) for $|+\rangle \leftrightarrow |-\rangle$ can be explained by the larger ESR inhomogeneous width.[11] Inhomogeneous broadening reduces the effective density of spins with mutually equal energy spacing. The solid curves in Figs. 4(a) and 4(b) are calculated ones. The value of 0.5 ms is insensitive to the choice of the other two parameters as long as they are much longer than 0.5 ms. Although it is difficult to determine the shape of the relaxation function from this work, a theory suggests that SSR should have a shape $\exp(-\sqrt{t/T_{ss}})$, where T_{ss} is a $1/e$-decay time.[12]

The optical energy transfer[13] at this concentration is considered to be much slower than the SSR.

For a more dilute sample (0.0034 wt.%) the side hole was not found in the same time region, which indicates that the origin of the side hole is in the SSR due to Cr-Cr interactions and not in the SLR in $\bar{E}(^2E)$. The magnetic dipole-dipole interaction between Cr spins is most probably responsible for the SSR.

In summary, we have measured the SSR time due to flip

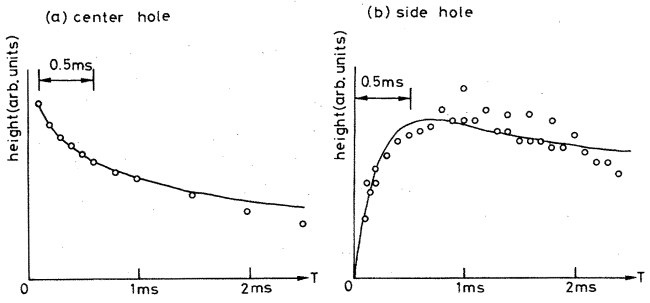

FIG. 4. Decay of the center hole (a) and the growth of the side hole (b) by SSR detected by using the pulse sequence in Fig. 2(b). Open circles indicate observed hole heights and the solid curves are calculated ones from rate equations assuming that SSR time is 0.5 ms.

flop of like spins in an impurity ion solid by optical means and showed that the SSR time, which is the time required for the establishment of the internal equilibrium of the spin system, was much longer than the TR time. A small number of ions and their spins associated with a definite optical transition frequency are used as a marker for the detection of the SSR. Although the principle of the method is simple, a variety of fundamental information about spin thermodynamics which cannot be obtained by usual magnetic methods can now be obtained by this technique. If two stable tunable lasers are available, center and side holes with arbitrary separation can be detected easily, which greatly extends the range of application.

The present work is related to the study of microscopic mechanisms of optical dephasing process. In a previous paper[14] we reported that the contribution of the flip flop of the frozen core nuclei to the optical dephasing of ruby R_1 line is negligible. The present work adds the new information that the homogeneous broadening ($\gtrsim$ MHz) of R_1 line is not a lifetime broadening ($\lesssim$ kHz) due to SSR by Cr-Cr interactions. However, the detailed mechanism of the dephasing process of R_1 line is left unexplained.

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