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GROUND-STATE SPIN MEMORY IN THE $\bar{E}(^2E)$ LEVEL OF RUBY IN OPTICAL PUMPING VIA THE BANDS

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We wish to present direct experimental evidence of the retention of ground-state spin memory in the $\bar{E}(^2E)$ level of ruby under broadband optical pumping. This has been done by observing a change in the relative populations of the Zeeman components of $\bar{E}(^2E)$ when the populations of the ground-state ($^4A_2$) spin levels are readjusted by microwave saturation.

Recent experiments on excited state epr in the $\bar{E}(^2E)$ state of d^3 ions in corundum have indicated preferential populating of the Zeeman levels of metastable states in pumping through higher broad-absorption bands.[1,2] The evidence for this selective pumping is that one can observe epr in excited states (therefore implying a population difference between the Zeeman levels) in spite of the fact that spin-lattice relaxation between these levels is much slower than the radiative decay. In effect, at very low temperatures the levels cannot thermalize before they radiate and, therefore, must have been preferentially populated. Further corroborating evidence is had from the direct measurement of the intensity of fluorescent lines emanating from these Zeeman levels, which indicated that the excited-state spin temperature differed from the lattice temperature.[3] The existence of this preferential population in the absence of spin-lattice relaxation is not in itself sufficient evidence to indicate a spin memory from the ground state, for such preferential pumping could also come about by thermalization in higher-lying levels which feed the $\bar{E}$ state. In general, one might not anticipate a spin-lattice relaxation time in these higher levels which is fast compared to the feeding time of the metastable state; in ruby, for example, this feeding time from $^4T_2 \to {}^2E$ has been experimentally shown to be approximately 10^{-7} sec.[4] However, an experiment of the type reported here, where a change in the relative populations of the ground-state Zeeman levels by microwave saturation produces a change in the relative populations of the $\bar{E}$ Zeeman levels, seems to demonstrate unambiguously this spin memory.

In Fig. 1 is shown the Zeeman splitting of the $\bar{E}(^2E)$ and $^4A_2$ states. With H parallel to the c axis, pumping from the $^4A_2$ to $^4T_2$ preserves m_S. Spin memory would now imply that spin selection rules are operative in the multiphonon cascade from the $^4T_2$ band to the final metastable-doublet level without any intervening thermalization in any of the intermediate states. Since the spin-orbit perturbation must be involved in order to make the transition from quartet to doublet, we would anticipate a $\Delta m_S = 0, \pm 1$ selection rule in the $^4T_2 \to {}^2E$ cascade, considering the admixture of $^4T_2$ to ^2E to first order in spin-orbit coupling. This will, therefore, also be the selection rule from $^4A_2$ to the ^2E via the $^4T_2$. We make no assertions about the details of the cascade process or intermediate states which may be involved, such as the $^2T_1$.[5,6]

The spin populations in the Zeeman levels

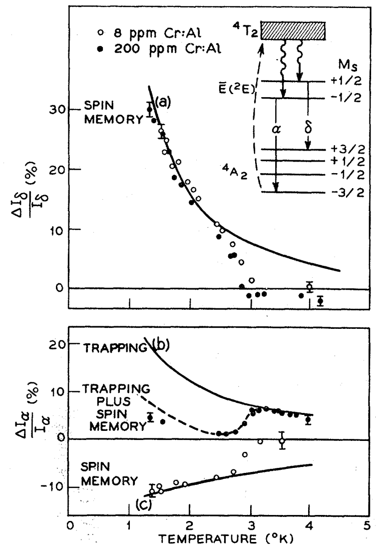

FIG. 1. Fractional change of intensities of α and δ lines observed when the ground-state $-\frac{1}{2}\rightarrow-\frac{3}{2}$ transition is saturated with microwaves. Curves (a) and (c) are proportional to the Boltzmann difference of population between the $-\frac{3}{2}$ and $-\frac{1}{2}$ ground states, where each curve has been adjusted to fit one low-temperature data point. Curve (b) is extrapolated from the high-temperature data points for the α line in the concentrated sample and is what is expected for trapping alone. At approximately 2.6°K, the spin-lattice relaxation in $\bar{E}$ becomes faster than the radiative lifetime and begins to mask the spin memory.

of $\bar{E}$ are monitored by observing the intensity of the α and δ fluorescent transitions as shown. The presence of reabsorption of the fluorescent light by ground-state ions, which becomes selective[7] when ground-state splittings are comparable to kT, also influences the intensities of α and δ and must be separated from the true spin-memory effects. The points in Fig. 1(a) and 1(c) indicated by open circles refer to data taken on exceedingly dilute ruby, i.e., 8 parts in 10^6 Cr per Al. In this low concentration, auxiliary experiments indicate that trapping is negligible. Spin-memory effects will only be observed, of course, at such low temperatures that the spin-lattice relaxation time is longer than the radiative lifetime. This occurs in the $\bar{E}(^2E)$ state of ruby below 3°K.[1]

The single crystals of ruby were mounted in a 48-kMc/sec microwave cavity with the external magnetic field along the c axis. The ruby was pumped from an Osram HBO-200 Hg lamp in a broad band centered at the $^4T_2$, using unpolarized light through a hole in the base of the cavity. The fluorescent Zeeman components were monitored with a high-resolution Jarrell-Ash one-meter spectrometer through horizontal slits cut in the cavity wall. With fixed microwave frequency, the magnetic field is swept through a ground-state resonance saturating it, and the change in monitored light intensity of the α or δ component is observed. The outstanding, pertinent experimental fact is that when the $-\frac{3}{2}\rightarrow-\frac{1}{2}$ ground-state transition is saturated, the intensity of the α line decreases while the intensity of the δ line increases, indicating an increase in the population of the $m_S=+\frac{1}{2}$ level relative to the $m_S=-\frac{1}{2}$ level in the excited $\bar{E}$ state. This change in the population ratio is what is expected from the simple spin selection rules $\Delta m_S=\pm1, 0$.[8] The size of the above-mentioned changes in intensity of α and δ will depend upon the difference in population, ΔN, between the $-\frac{3}{2}$ and $-\frac{1}{2}$ ground-state levels. It will also be a function of the relative efficiency of the $\Delta m_S=0$, and ±1 pumping transition probabilities. With increasing temperature this population difference decreases, and so will the change in δ and α intensities with microwave saturation. Curves (a) and (c) show how one expects these intensity changes to vary with temperature, assuming a Boltzmann distribution before complete microwave saturation, where the curves have been fitted at a single low-temperature point.[9] The experimental points indicated by open circles follow this expected variation up to approximately 2.6°K. This is the temperature at which the spin-lattice relaxation time in $\bar{E}$ becomes comparable with the radiative lifetime[1] and rapidly begins to exceed it, so that spin-memory effects are not exhibited.

In a more heavily doped sample of ruby, reabsorption of α is no longer negligible. Now, saturation of the $-\frac{3}{2}\rightarrow-\frac{1}{2}$ ground-state transition reduces the population in the $-\frac{3}{2}$ level, which reduces the trapping of the α line, thereby increasing its intensity. This effect in the concentrated sample, which is opposite in sign to the spin-memory effect, is shown in curve (b). This curve is the change in α intensity expected due to trapping as observed by monitoring the α intensity above 3°K in the absence of microwave power. Below 3°K the spin-memory effects set in and operate in conjunction with trapping. The dotted curve is that expected from the sum of spin-memory effects as determined in the dilute sample plus the trapping effects seen in the more concentrated sample. The experimental points are in essential agreement with the expected change from these two effects.

Even in the more concentrated sample at 48 kMc/sec and very low temperatures, the population of the $+\frac{3}{2}$ state is so low that trapping is negligible for the δ line. This is seen in the figure, where the observed fractional change in δ intensity for the concentrated sample (indicated by dark points) is seen to coincide with that observed on the more dilute sample. As one approaches higher temperatures and begins to populate the $+\frac{3}{2}$ level, reabsorption effects should appear, and it is likely that the slight difference between the experimental points for the δ line for the two samples above 3°K is attributable to such effects.

Changes in α and δ intensity were also observed when the $-\frac{1}{2}\rightarrow+\frac{1}{2}$ and $+\frac{1}{2}\rightarrow+\frac{3}{2}$ transitions were saturated. The observed changes were all consistent with the above notions of spin memory and trapping, assuming that the ground-state $\Delta m_S = \pm 2$ spin-lattice relaxation transitions are faster than the ground-state $\Delta m_S = \pm 1$, 0 relaxation rates. This is to be expected from examination of the phonon coupling constants given by Donoho for ruby.[10]

One would expect that this phenomenon of spin memory is fairly general and not restricted to ruby. Some such effect would explain the ability to detect excited-state epr in the $\bar{E}(^2E)$ state of Mn^{4+} in Al_2O_3 at temperatures sufficiently low such that T_1 in this state is longer than the radiative lifetime.[2] Very recently, selective population of the Zeeman components of the excited $E_{5/2}$ metastable state has also been observed in CaF_2:Tm^{2+} by Anderson and Sabisky.[11] As pointed out by these authors, this selective populating of the excited state is qualitatively consistent with partial transfer of ground-state magnetization to the excited state. We feel that the detailed quantitative results given here for ruby, relating the change in excited-state magnetization to the redistribution of the ground-state population by microwave saturation, clearly distinguish spin-memory effects from other conceivable causes of preferential populating of the excited state.

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[9]It is of course realized that in saturating these two levels, the change of population in each is not exactly $\Delta N/2$, half the Boltzmann difference. This is so because of relaxation into these levels from the $+\frac{1}{2}$ and $+\frac{3}{2}$ states. However, we do not feel that the changes are appreciably different from $\Delta N/2$ for the following reasons. First, the vast majority are in the lower states at this value of field and over a good portion of the temperature range covered. Second, since the strongest ground-state relaxations are the $\Delta m_S = \pm 2$, the tendency to increase the $-\frac{3}{2}$ level via this relaxation from the $+\frac{1}{2}$ level will be offset by the decrease in the $-\frac{1}{2}$ level by the corresponding $\Delta m_S = +2$ relaxation to the $+\frac{3}{2}$ level, so that the total population in $-\frac{3}{2}$ and $-\frac{1}{2}$ levels will not change appreciably during saturation.

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