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EXCITED STATE ELECTRON SPIN RESONANCE USING NON-RESONANT FLUORESCENCE LINE NARROWING

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Abstract. Non-resonant fluorescence line narrowing (FLN) is used to examine resonances between excited states of ions. We discuss resonances between crystal field states in ruby, alexandrite and LaF$_3$:Pr$^{3+}$ and between Zeeman sublevels in LaF$_3$:Er$^{3+}$. We show that the latter is equivalent to excited state ESR, over which it can have many advantages.

I. INTRODUCTION.

The linewidths in non-resonant fluorescence line narrowing (FLN) experiments are often inhomogeneously broadened because their crystal field energy levels depend on many crystal field parameters, in a different way for each state, so that while a pair of sites in slightly different environments may have one transition energy in coincidence, it is unlikely that they will have more than one in coincidence/1/. An exception occurs when a pair of excited levels arise from the same crystal field state as for example the sublevels of a Kramers ion split by a magnetic field. In this case, the inhomogeneous contribution to the non-resonant FLN spectra will contain only the contribution to the resonance width due to the distribution of $g$-values over the ions probed with the laser. In this paper we discuss the use of non-resonant FLN to examine two types of excited state resonances: (1) between crystal field levels of an ion, in order to obtain the phonon resonance widths which occur in excited state relaxation, and (2) between the Zeeman sublevels of Kramers ions, which is the equivalent of high field ESR.

II. EXPERIMENTS.

A single frequency scanning cw dye laser is used to excite either one of the higher lying crystal field levels above a metastable state or the upper of a pair of Zeeman levels of an ion in a magnetic field. The excited ions relax to the lower level, typically with a relaxation time $T_1$=100ps (upper crystal field level) or $T_1$=10μs (upper Zeeman sublevel). Fluorescence from the lowest metastable level is analyzed with a Fabry-Perot interferometer as shown in Fig. 1. A single fluorescence line is isolated with a 0.75m monochromator and is detected with a photomultiplier. Single photon events are registered on a counter and the number of events in a 1ms time interval is stored sequentially in 250 memory locations of an LSI-11 computer as the interferometer is scanned over about two free spectral ranges. The spectrum is scanned about 100 times to signal average the data.
III. EXAMPLES OF CRYSTAL FIELD RESONANCES.

A. $\text{Al}_2\text{O}_3$:Cr$^{3+}$ (ruby). The $E \rightarrow 2A$ excited state resonance of the $^2E$ state of ruby is of great interest as a monochromatic source of phonons. Its resonance width has been measured from studies of the phonon dynamics in a magnetic field/2/ and by excited state far infrared absorption/3/.

We excited the $^4A_2 \rightarrow ^2E$ transitions in a magnetic field of 29.75kG as shown in Fig. 2. The instrumental resolution was 310MHz. Pumping the $E$ level and viewing the luminescence to the $^4A_2(-3/2)$ highest ground state Zeeman level (middle spectrum) gave an additional linewidth of 370MHz, the $3/2 \rightarrow -3/2$ inhomogeneous resonance width. This resonance is inaccessible in ESR since it is a $\Delta M_z = 3$ transition. When the lower Zeeman sublevel of $2A$ was pumped, an increase in the linewidth of 450MHz was observed (right spectrum). This yields, for a Gaussian $2A \rightarrow E$ resonance, a width of 450MHz; for a Lorentzian, 780MHz. For a Voigt profile, our measurement yields a width between these values and is consistent with the 570MHz result of Lengfellner/3/. Our data does not justify a more complete lineshape analysis at this time.

B. BeAl$_2$O$_4$:Cr$^{3+}$ (alexandrite). We obtained FLN spectra of alexandrite in zero magnetic field. Goossens/4/ had obtained a value for the $2A \rightarrow E$ resonance width of 2.1GHz from a study of the phonon dynamics in a small field. Our FLN results (Fig. 3) yield a much larger value of 13.9GHz. The discrepancy may result either from sample differences or the occurrence of energy transfer during the 1.32ms radiative lifetime. Also seen is the $^4A_2$ ground state splitting which we measure to be 6-18.9GHz compared to 16.2GHz reported by Walling/5/.

![Fig. 1 Schematic of the non-resonant FLN apparatus.](image)

![Fig. 2 Non-resonant FLN spectra of ruby for two non-resonant transitions (finesse = 8 and FSR = 2.5GHz).](image)

![Fig. 3 Non-resonant FLN spectrum of alexandrite.](image)
Fig. 4 Excitation spectrum of the $^3H_4(I)\rightarrow^1D_2(II)$ transition of Pr$^{3+}$ in LaF$_3$ (solid circles) and non-resonant FLN linewidth (open circles) viewing fluorescence from $^1D_2(I)$ as a function of laser frequency relative to $v_0$, the line center of the $^1D_2(II)$ transition.

IV. HIGH FIELD ESR.

As an example of the application of FLN to high field ESR we consider LaF$_3$:Er$^{3+}$. The single frequency cw dye laser was tuned to excite the $^4I_{15/2}\rightarrow^4F_{9/2}$ transition of Er$^{3+}$ in a large magnetic field parallel to the c-axis (inset Fig. 5). The excitation spectrum of the absorption to the lower and upper Zeeman levels have inhomogeneous widths of 1.68 and 2.08 GHz, respectively.

LaF$_3$ is complicated by the presence of six magnetically inequivalent sites. The non-resonant FLN spectrum under low resolution (FSR 10 GHz) is shown in Fig. 5. Because of the large anisotropy of the g-tensors of the ground and

![LaF$_3$:Pr$^{3+}$](image1)

![LaF$_3$:Er$^{3+}$](image2)
excited states only a small misalignment splits the spectrum into three resolvable groups of sites.

The FLN spectrum under high resolution (FSR 1.5GHz, instrument resolution 70MHz) appears in Fig. 6. The direction of the magnetic field was carefully aligned along the c-axis to minimize the effect on the FLN linewidth of the inequivalent sites. Fluorescence to the lower (spectrum A) and upper (spectrum B) Zeeman levels of the ground state were isolated with the spectrometer. The width of the FLN spectrum of fluorescence to the upper level is broader than that to the lower level, and this additional width of 90MHz is the resonance width of the ground state, corresponding to an ESR linewidth of 7.8G.

The magnetic field dependence of the linewidth for the fluorescence to the lower Zeeman level, after subtraction of the instrumental width, is shown in Fig. 7. This is the \( ^4\!F_{9/2}(I) \) Zeeman resonance width and extrapolates to 70MHz at low fields. There are several factors which can contribute to the increase in linewidth with field: (1) inhomogeneity of the magnetic field over the 0.1mm\(^3\) viewing volume, estimated as <100MHz at 30kG, (2) slight misalignment of the field relative to the c-axis producing a small residual splitting due to the magnetically inequivalent sites, estimated as <50MHz at 30kG, and (3) an actual increase in the linewidth at higher fields. Thus the major portion of the observed increase in linewidth (130MHz) is probably experimental.

The low field (3.2kG) g-values of the ground state for \( H//C \) was measured to be 8.22±0.07, which compares with values in the literature of 8.12±0.09/8/ and 7.5±0.4/9/. The g-value of the \( ^5\!F_{9/2}(I) \) excited state was determined with great accuracy at high fields (-30kG) as 3.650±0.002. With FLN one probes a subset of ions within the optical inhomogeneous line. In Fig. 8 we show the small but systematic dependence of the g-value on location within the inhomogeneous profile.

V. CONCLUSIONS.

Non-resonant FLN has been used to do ground and excited state resonance spectroscopy with resolution comparable to ESR but at frequencies outside the range of standard techniques. The advantages are major and include (1) the ability to work at very high resonance frequencies without the need of ultra-high frequency microwaves, (2) the sensitivity inherent in optical detection techniques (especially...
useful for excited state ESR), and (3) the ability to study a select group of ions within the inhomogeneous absorption profile and within a small spatial volume of the sample.

We found for LaF₃:Er³⁺ that the high field spin resonance linewidths are very narrow. As a result, experiments in stimulated phonon emission between the Zeeman sublevels/10/ must be carried out on samples oriented to better than 0.1° in order that phonons generated on one of the six magnetically inequivalent sites are in resonance with the other sites.

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