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Ultrasensitive optical spectroscopy of rare earth solids

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Abstract

In this paper, we report recent work wherein f→f transitions have been observed in samples either too dilute or too opaque to have been studied previously. Ultrasensitive reflection and fluorescence spectra are discussed together with techniques for the fabrication of thin film samples with enhanced rare earth absorption. Results described include, the observation of absorption lines in the spectra of epitaxial films containing less than one layer of absorbing ions, the observation of sharp lines in the spectra of rare earth semiconductors and metals, and the preliminary observation of frequency dependent structure in the inhomogeneously broadened fluorescence of Eu^{3+} at 10–100 ppb concentration in a silica glass fiber.

1. Introduction

The observation of sharp optical spectra is one of the most useful tools for the study of matter. In particular, the visible spectra of tripositive lanthanide ions typically contain numerous sharp lines corresponding to transitions within the 4f subshell. Unfortunately, intraconfigurational transitions are forbidden to the degree that parity conservation holds, and 4f orbitals are well shielded from the outside environment. As a result, even in the most asymmetric solids, oscillator strengths for these f→f transitions rarely exceed 10^{-6}. Because of this small oscillator strength, past observations of these sharp spectral lines in solids have always required the study of macroscopically thick samples.

This paper is a report of recent work wherein f→f transitions have been observed in samples too thin, too opaque, or too dilute to have been studied previously. Results involving the observation of sharp absorption lines in the spectra of epitaxial films containing less than one layer of absorbing atoms [1] and in the spectra of opaque semiconductors and metals [2] are described. Preliminary results involving the measurement of fluorescence from small numbers of ions are also described.

2. Ultrasensitive absorption spectroscopy

The ultrasensitive spectrophotometer constructed for these experiments consists of a standard tungsten-halogen lamp for illumination, an interchangeable sample optical cryostat, a grating spectrograph, and a photodiode array detector. With careful optimization, this system is capable of reaching signal-to-noise ratios above 10^5 for transparent samples. An improved system currently under construction is expected to be more than an order of magnitude more sensitive.

2.1. Ultrathin samples

Three types of NdF_3 films were prepared by molecular-beam epitaxy and studied with the spectrophotometer. The first type were films with a thin protective overcoat of transparent LaF_3 on a NdF_3 layer grown on a GaAs substrate. It was found that additional sensitivity could be gained by using a second set of films which featured a LaF_3 overcoat on a NdF_3 layer on a LaF_3 buffer layer grown on GaAs. The thickness of the LaF_3 buffer layer was designed such that multiple reflections enhanced the intensity of the absorption lines in the NdF_3 [1]. Alternatively, the NdF_3:LaF_3:GaAs system can be considered as a quarter-wavelength cavity with an electric field node at the GaAs surface and an antinode

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at the NdF_3 layer with the increased absorption proportional to the intensity of the antinode. Films with NdF_3 thicknesses down to one monolayer were prepared and studied. One unit cell of NdF_3 as grown for these samples is approximately 7.2 Å in thickness and contains two layers of Nd ions. The third type of film was developed to study the nature of the film–air interface and featured LaF_3 overcoats on one or two monolayers of NdF_3 on a LaF_3 buffer layer grown on GaAs. The thickness of the LaF_3 overcoats ranged from eight layers down to no overcoat.

With films of the first type, NdF_3 grown directly on GaAs, it was established that the lineshape and line strength were strongly dependent on the thickness of the NdF_3 layer [1]. The various asymmetric lineshapes observed agree quite well with a theoretical model which stresses the effect of the narrow resonances on both the optical thickness of the NdF_3 layer and the Fresnel coefficients at the interfaces. For these films, there was a clearly observable increase in the linewidth as the films became thinner. Because of the increased broadening, no lines were observable in films containing less than 50 Å of NdF_3, approximately 7 unit cells.

With films of the second type, NdF_3 on a LaF_3 buffer layer, the strength of these absorption lines was sufficiently enhanced that absorption from a single layer of Nd ions was observable (Fig. 1(a)). By studying a series of films of differing thicknesses, it was established that the splitting and positions of the two lines in Fig. 1 show a clear dependence on the thickness of the NdF_3 layer. This is believed to result from the NdF_3 lattice expanding in the *a–b* plane to accommodate the surrounding LaF_3 layers.

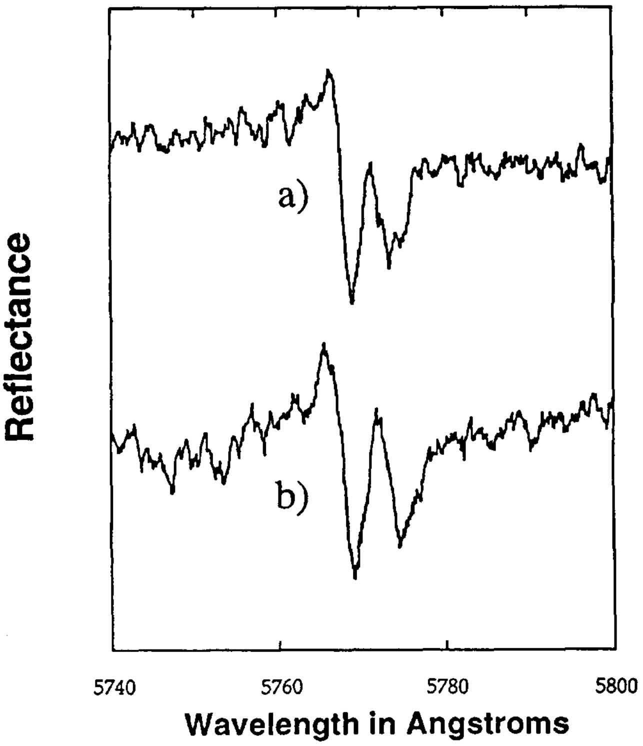

Fig. 1. Reflection spectra of a submonolayer of NdF_3 on LaF_3 on GaAs: (a) with a thick protective overlayer of LaF_3; and (b) with a single atomic layer overcoating.

Once the ability to observe absorption produced by a single layer was demonstrated, it was realized that this technique could be used as a layer-by-layer probe of the crystal structure of a solid. As proof of this concept, we studied the films of the third type, each of which contained a single layer of Nd ions with the distance between this layer and the surface varying from film to film. For films with a single layer of NdF_3 overcoated with only one atomic layer of LaF_3, absorption lines are easily observable (Fig. 1(b)). However, these absorption lines are completely unobservable for a single layer of NdF_3 on the surface, *i.e.* with no overcoat. It is believed that this results from the formation of an amorphous surface layer due to exposure of the film to atmospheric oxygen and water vapor.

2.2. Opaque samples

The compound $(Nd,Ce)_2CuO_{4-x}$, one of the class of perovskite high T_c superconductors, was chosen for a study of opaque materials for a variety of reasons [2]. First, it has both semiconducting and metallic phases depending on the level of Ce^{4+} doping. The cerium-free compound is an opaque semiconductor, but with 7.5% doping and slight reduction in oxygen, the material becomes a highly anisotropic metal which is a superconductor below ≈ 25 K. Also, the Nd ions in this material are to a degree isolated from the conduction electrons which are restricted to planes above and below the rare earth site. Finally, the material contains Nd ions surrounded by an asymmetric array consisting mainly of oxygen ions. This combination results in a strong series of spectral lines similar in nature to those observed in Nd oxides.

Six $(Nd,Ce)_2CuO_{4-x}$ samples were studied in detail. Three were randomly oriented polycrystalline pellets with 0%, 4% and 7.5% of the neodymium replaced with cerium, and a fourth was an oriented undoped film. The other two samples studied in detail were oriented metal (7.5% cerium doped) films. Spectral lines resulting from f→f transitions were observed in all of these samples. These spectra are believed to include the first observation of f→f transitions in a metal using optical spectroscopy.

The most significant results of these studies were the observed differences in relative intensities and broadening of lines in the undoped and doped samples. In particular, the reflection spectra of the doped and undoped thin film samples differed dramatically. The replacement of certain Nd^{3+} ions by Ce^{4+} ions should increase the asymmetry of nearby Nd sites which will increase the oscillator strength at these sites. These high oscillator strength sites are inherently located near defects so the increased line strength goes into the wings of the lines producing extreme broadening. This additional broadening was masked in the less crystalline powder samples. To adequately understand the reflection spectra, it was essential to realize that the amplitude of reflection depends on the mismatch in indices of refraction at an interface. The addition of a resonant absorption to the index of refraction of a material can produce quite complex changes in the spectrum of reflected light. In particular, for a Lorentzian absorber, any symmetric or asymmetric Lorentzian lineshape is possible depending on the value of the background, non-resonant indices. The dramatic but superficial differences exhibited by the reflection spectra indicate that the indices of refraction for the metallic and insulating samples are different.

3. Ultrasensitive fluorescence spectroscopy

The first goal of the ultrasensitive fluorescence experiments is the observation of statistical fine structure (SFS) in the fluorescence spectra of glass fibers. Once these studies are completed, refinements in the experimental setup are expected to lead to the observation of individual rare earth fluorescence centers. If a glass matrix contains a very dilute level of activators and an excitation laser is focused down so that it interacts with a small volume of material, it is possible to reach conditions in which the total distribution of inhomogeneous sites is no longer sampled. This was initially demonstrated in crystalline solids [3,4]. In addition, the number of resonances per unit frequency can be minimized by studying systems with a large ratio of inhomogeneous to homogeneous linewidths as in a highly doped glass fiber [5]. Under these circumstances, the spectrum observed is produced by a small random sampling of the disorder distribution, resulting in statistical fine structure. We have investigated Eu^{3+} activated pure-silica glass with a ratio of inhomogeneous to homogenous broadening of approximately 10^5. Statistical fine structure was observed in the fluorescence excitation spectra, and the amount of structure is correlated to the location in the Gaussian inhomogeneous line. An estimate of the number of ions involved is obtained by comparing the observed spectra with simulated spectra generated using a statistical model.

Activated optical fibers provide us with an ideal configuration with which to measure SFS. The intentional doping of the core creates a minute excitation region, and the fiber naturally produces an efficient channel for the collection of the excited fluorescence of the centers. The concentration of Eu^{3+} in the sample considered here is between 10 and 100 ppb. A small interaction volume is obtained by exciting the fiber perpendicular to the waveguide with a laser beam waist of less than 5 μm. The focal point of the laser is locked to a certain location on the fiber. Other components of the experimental setup include an argon laser, a single-frequency ring dye laser with a long-term stability of better than 5 MHz [6], a liquid helium immersion optical cryostat and high efficiency collection optics which transmitted the light signal to a low dark-count high quantum-efficiency photomultiplier tube. Two choppers operating 180° out of phase are used to prevent laser light reaching the photomultiplier tube [7]. This chopping technique also limits any short-lived spurious luminescence signals. A bandpass filter is used to select the desired $^5D_0 \rightarrow {}^7F_2$ fluorescence.

Detailed excitation spectra for two sections of the inhomogeneously broadened $^7F_0 \rightarrow {}^5D_0$ transition are given in Figs. 2 and 3. In each of these spectra, the laser is scanned over a 5 GHz range in steps of 100 MHz. The solid line drawn through the points is merely a guide for the eye. The homogeneous linewidth of this transition of Eu^{3+} in silicate glass at 2 K ranges from less than 50 to greater than 100 MHz [8]. The structure observed is both spatial and frequency dependent. By comparison, the spectrum of a bulk sample would be flatter over this frequency interval because of the large number of ions involved, and the statistical fine structure would be below the noise level. In the figures, the noise level associated with the counting statistics is represented by a partially shaded bar located at the mean of the observed data. It is apparent that there is structure than cannot be attributed to counting statistics. In addition, the SFS shown in Fig. 2 was

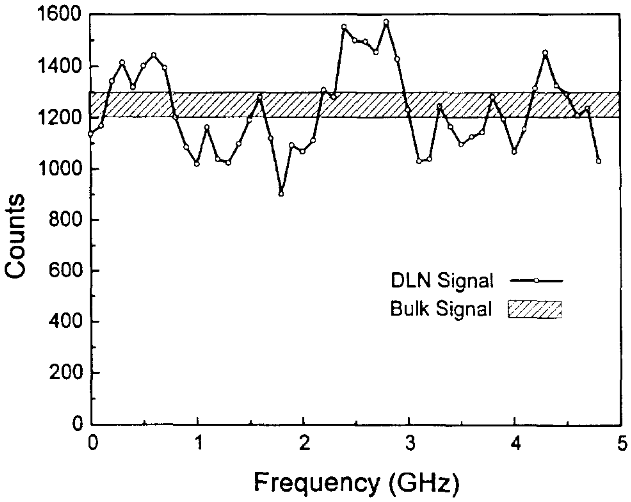

Fig. 2. High resolution excitation spectrum of the $^7F_0 \rightarrow {}^5D_0$ transition of Eu^{3+} ions in a silica fiber measured at 17 254 cm^{-1}. The horizontal bar represents the amount of variation that would be expected in the absence of observable statistical fine structure, *i.e.* the Poisson counting error.

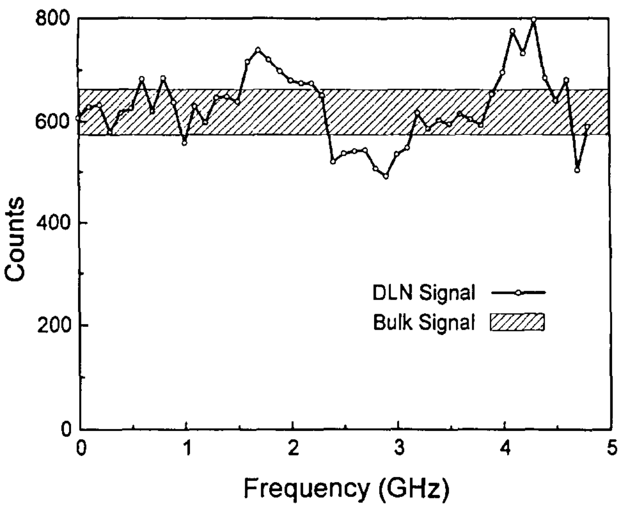

Fig. 3. High resolution excitation spectrum of the Eu^3 doped silica fiber obtained at 17 200 cm^{-1}. The horizontal bar represents the amount of variation that would be expected in the absence of observable statistical fine structure, *i.e.* the Poisson counting error. This spectrum is believed to contain a significant contribution from background fluorescence.

observed in four separate data runs taken over a period of 2 h.

An estimate of the number of ions involved can be obtained by simulating an excitation spectrum. Over the relatively narrow range of 5 GHz, the Gaussian distribution of resonance frequencies is approximately uniform. A random number generator was used to create sets of resonance frequencies. Excitation spectra were then generated by summing the corresponding Lorentzian lines. The three simulated spectra of Fig. 4 were generated using a homogeneous linewidth of 100 MHz and a total of 50, 500 and 5000 ions. The total count rate was normalized to match that of the data obtained at 17 254 cm^{-1} (Fig. 2). The horizontal bar once again represents the expected structure for a bulk sample, *i.e.* Poisson counting noise. It can be seen that the amount of statistical fine structure in Fig. 2 is consistent with the simulation involving 500 ions, *i.e.* a spectral density of one ion per 10 MHz. The scan recorded at 17 200 cm^{-1-} has a considerably reduced count rate so that it undoubtedly involves fewer ions. Unfortunately, at this point, the signal from the Eu^{3+} ions is somewhat masked by a broad background fluorescence which is not completely eliminated by our experimental arrangement.

In conclusion, we have shown that using ultrasensitive techniques, it is possible to observe f→f transitions in systems previously thought to be beyond the realm of optical spectroscopy. These systems include metals and other opaque solids, as well as insulators containing very small numbers of rare earth ions.

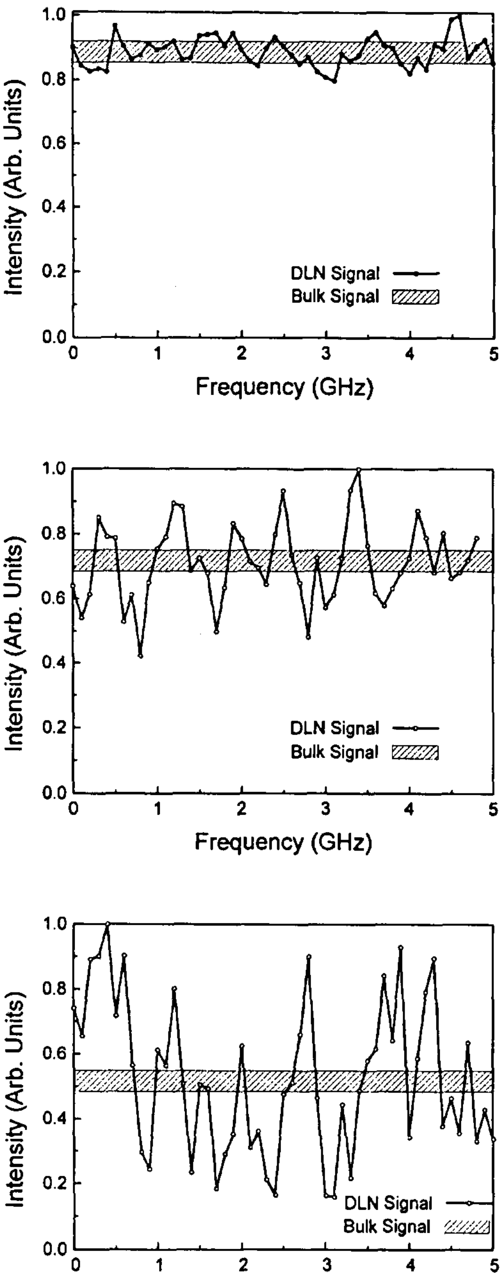

Fig. 4. Simulated excitation spectra of the Eu^3 doped silica fiber consisting of (a) 5000, (b) 500 and (c) 50 ions with randomly distributed center frequencies. The width of the shaded area is equivalent to the counting error for the data obtained at 17 254 cm^{-1} (Fig. 2).

Acknowledgments

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