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Spectroscopic properties of excited states of ions in glass measured using laser-induced fluorescence line narrowing

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Laser-induced fluorescence-line-narrowing techniques are extended to measure site-to-site variations in the spectroscopic properties of excited states of optically active ions in glass. The crystalline Stark splitting associated with the initial excited state, rather than the terminal fluorescence state, is observed. The process is illustrated for Eu^{3+} in a lithium-borate glass by exciting the $^5D_1$ state and observing $^5D_0 \rightarrow {}^7F_J$ fluorescence. The measured crystal-field splitting of $^5D_1$ is in good agreement with that predicted from the splitting of $^7F_1$. Conditions necessary for obtaining fluorescence line narrowing in excited states are discussed.

I. INTRODUCTION

Recently, Brecher and Riseberg[1] used the technique of laser-induced fluorescence line narrowing to probe the environment surrounding rare-earth ions in glasses. Due to the large site-to-site variations in the local crystalline electric field, paramagnetic ions in glass have broad inhomogeneous optical linewidths. However, with the aid of tunable narrow-band lasers it is possible to excite selectively only a small subset of ions whose energy levels are in resonance with the laser. The resulting fluorescence linewidths are narrower than the full inhomogeneous widths. By scanning the lasing frequency, all sites can be sampled. From the positions of the line-narrowed structure as a function of excitation wavelength, simple crystal-field theory has been applied to derive parameters that describe the different local environments.[1] The Eu^{3+} ion has been particularly useful for these studies because its first excited state, $^5D_0$, is a singlet, and the structure in the fluorescence is determined solely by the terminal-ground-state splittings.

In the case in which the excited state is not a singlet state, but consists of several closely spaced Stark components, accidental coincidences of levels can occur.[2,3] The spectral overlap of components from ions at different sites results in the simultaneous excitation of many subsets of ions. The resulting nonresonant fluorescence consists of multiple overlapping spectra with greatly decreased resolution, which makes any detailed analysis difficult. Useful experimental data may still be obtained only by pumping at the edges of the absorption band where the amount of overlap is minimal. Recently, an investigation of the fluorescence resulting from narrow-band excitation of the $^5D_1$ band of Eu^{3+} in a lithium-borate glass revealed that the fluorescence spectra were well resolved at all excitation wavelengths. This enabled us to measure the variations in the energies of the $^5D_1$ Stark components and to identify all of the fluorescence lines.

II. EXPERIMENTAL

The samples investigated were melted at the N. B. Stand. (U. S.) and consisted of lithium-borate glass doped with a 1-mol% Eu_2O_3. Excitation was accomplished with a pulsed nitrogen-laser-pumped dye laser and a Coumarin 485 dye. To reduce the possibility of energy transfer occurring between Eu ions at dissimilar sites, all flourescence spectra were recorded within 150 μsec after pulsed excitation and the sample was maintained at 1.7 K throughout. Further details of the experimental techniques and apparatus used are given in Ref. 4.

The full inhomogeneous width of the $^7F_0 \rightarrow {}^5D_1$ absorption band is approximately 200 cm^{-1} and centered at 19100 cm^{-1}. The three-line Stark structure of $^5D_1$ is unresolved. Fluorescence spectra were taken at 20-cm^{-1} intervals across the $^5D_1$ absorption band; the spectral resolution was <7 cm^{-1}. Examples of these spectra are shown in Fig. 1. Ions initially in the $^5D_1$ state decay nonradiatively in <1 μsec to the $^5D_0$ state, from which fluorescence to the various ^7F_J states occurs. For low excitation frequencies the fluorescence shows a basic similarity to the $^5D_0 \rightarrow {}^7F_J$ fluorescence obtained when the $^5D_0$ state is excited directly. The $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, and $^5D_0 \rightarrow {}^7F_2$ transitions are easily identified and are labeled in Fig. 1. At higher excitation frequencies a group of lines is observed whose positions and patterns

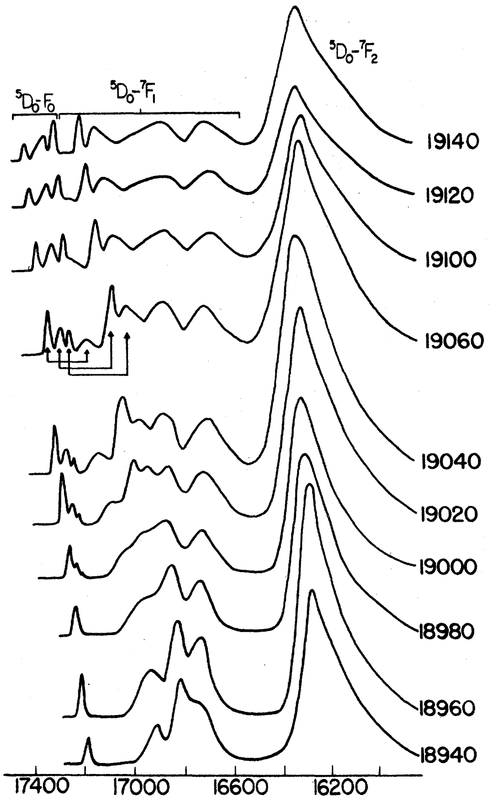

FIG. 1. $^5D_0 \rightarrow {}^7F_{0-2}$ luminescence spectra of Eu^{3+} in $60B_2O_3 \cdot 40Li_2O$ glass at 1.7 K as a function of excitation energy (cm^{-1}) in the $^7F_0 \rightarrow {}^5D_1$ absorption band. The correspondence between the $^5D_0 \rightarrow {}^7F_0$ lines and the $^5D_0 \rightarrow {}^7F_1$ ($\epsilon-$) lines is shown for the 19 060-cm^{-1} spectra.

of growth indicate that they are due to $^5D_0 \rightarrow {}^7F_0$ transitions. Additional lines also appear in the region of $^5D_0 \rightarrow {}^7F_1$ transitions.

III. DISCUSSION

To explain the luminescence behavior we propose the model given in Fig. 2, where the relative energies of the $^7F_0$, $^5D_0$, and three $^5D_1$ Stark components are shown for three Eu^{3+} ions in dissimilar sites. The patterns of the splittings are different, and increase in magnitude from left to right. The centers of gravity of $^5D_0$ and the $^5D_1$ set of levels move in energy in the same direction from site to site. The horizontal arrow shows the excitation energy in the $^5D_1$ absorption band. Radiative and nonradiative decays are shown by solid and dashed lines, respectively. At the lowest excitation energy only the lowest $^5D_1$ component will be in resonance with the laser, and the line-narrowed fluorescence will be characteristic of a single ion. This is observed for the $^5D_0 \rightarrow {}^7F_0$ transition in Fig. 1. As the excitation energy is increased, the $^5D_0 \rightarrow {}^7F_0$ line should move to higher energy, and at the same time a second and third $^5D_0 \rightarrow {}^7F_0$ line should appear in its place corresponding to other subsets of ions being simultaneously pumped via their second and third $^5D_1$ Stark components, respectively, as depicted in Fig. 2. This expected pattern of development is seen in Fig. 1 where the $^5D_0 \rightarrow {}^7F_0$ luminescence reveals a three-line structure and all of the lines move to higher energies with increasing excitation energy. The resolution in the luminescence depends critically on the splittings in the $^5D_1$ state and on the positions of the $^5D_0$ levels relative to those of the $^5D_1$ levels for different sites. If the energy of the $^5D_0$ level above the ground state does not vary much from site to site, then the $^5D_0 \rightarrow {}^7F_0$ fluorescence lines will overlap. In addition, complex spectra will be observed if the $^5D_1$ splittings are small or if the homogeneous linewidths are large.

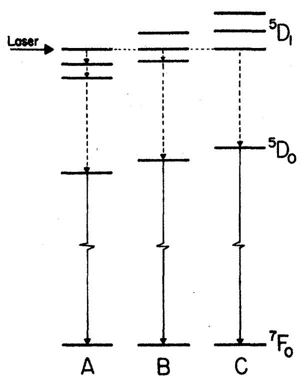

FIG. 2. Partial energy-level scheme of Eu^{3+} in a glass. Ions A, B, and C represent three subsets of ions which are in resonance with the laser via different $^5D_1$ Stark components. Solid and dashed lines denote radiative and nonradiative transitions, respectively. Only the $^7F_0$ level within the ^7F_J group of terminal levels is shown for simplicity.

Simultaneously with the appearance of additional $^5D_0 \rightarrow {}^7F_0$ lines, the $^5D_0 \rightarrow {}^7F_1$ fluorescence in Fig. 1 also begins to show extra structure at high energies. It is known[1,5] that in oxide glasses the transition from $^5D_0$ to $^7F_1(\epsilon-)$, where $\epsilon-$ denotes the lowest component of $^7F_1$, is more sensitive to changes in the local field than transitions to the other $^7F_1$ components; therefore, this transition is more likely to be resolved when ions in dissimilar sites are simultaneously excited. Hence we associate the new structure in the $^5D_0 \rightarrow {}^7F_1$ luminescence with this transition.

Following the procedure of Motegi and Shionoya,[6] the energies of the $^5D_0$ and $^7F_1$ states, obtained by pumping $^5D_0$ directly, are plotted in Fig. 3 as a function of $^5D_0$ excitation energy, which is re-

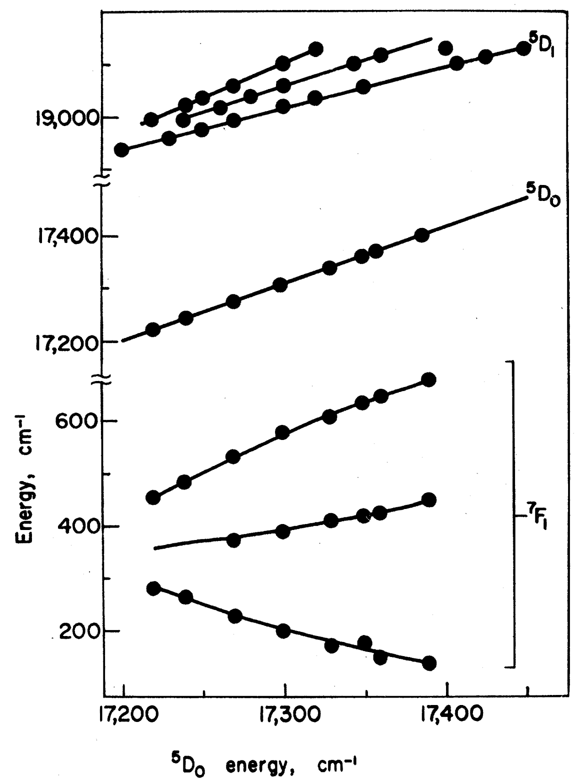

FIG. 3. Plot of the $^7F_1$, $^5D_0$, and $^5D_1$ energy levels of Eu^{3+} in $60B_2O_3 \cdot 40Li_2O$ glass at 1.7 K as a function of $^7F_0 \rightarrow {}^5D_0$ energy. The $^7F_0$ ground state is taken as the zero of energy.

garded as a parameter describing the local crystal-field strength at the Eu site. Also included in Fig. 3 are the projected positions of the $^5D_1$ Stark levels obtained from the positions of the $^5D_0 \rightarrow {}^7F_0$ transitions in Fig. 1. There is a strong similarity between the pattern of the splittings of the two $J=1$ states, $^5D_1$ and $^7F_1$ states. The ratio of the $^5D_1$ Stark splittings to those of $^7F_1$ is given by the ratio of the operator equivalent parameters $\alpha(^5D_1)/\alpha(^7F_1)$. From Judd's calculation,[7] a value of 0.298 was estimated. However, experimental evidence[8] indicates that this value is too large, a more realistic value being about 0.2. The discrepancy is due to the inadequacy of the Russel Saunders approximation used by Judd in his calculations. Comparison of the $^5D_1$ and $^7F_1$ splittings in Fig. 3 shows that the ratio of the splittings is very close to this value of 0.2 across the whole spectrum of sites, indicating the essential correctness of our model. The importance of the relative slopes of the $^5D_1$ curves in Fig. 3 in determining the extent to which ions in dissimilar sites are simultaneously excited is readily seen.

On the basis of this model, it is possible to identify the fine structure at the high-energy side of the $^5D_0 \rightarrow {}^7F_1$ luminescence in Fig. 1. The positions of these lines are plotted in Fig. 4 as a function of $^5D_0$ energy. From the positions of the $^5D_0 \rightarrow {}^7F_0$ lines in Fig. 1, the positions of the corresponding $^5D_0 \rightarrow {}^7F_1(\epsilon-)$ lines are calculated from Fig. 3 and are also plotted in Fig. 4. The comparison between the two sets of data shows that there is a line-for-line correspondence between the $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_1(\epsilon-)$ fluorescence. This correspondence is indicated in Fig. 1.

Several observations can be made on the basis of these results. First, it is seen from Fig. 1 that the relative intensities of the $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_1(\epsilon-)$ lines change drastically across the pump band. The intensity of the highest-energy component decreases with respect to that of the other lines as the pump energy is increased. As this line is a result of pumping the lowest $^5D_1$ Stark component, the number of ions resonant with the laser via this component decreases with increasing pump energy towards the high-energy side of the absorption band, and the resulting luminescence also decreases. Second, the intensity of the $^5D_0 \rightarrow {}^7F_1$ fluorescence as a whole decreases in intensity relative to that of the corresponding $^5D_0 \rightarrow {}^7F_0$ fluorescence with increasing pump ener-

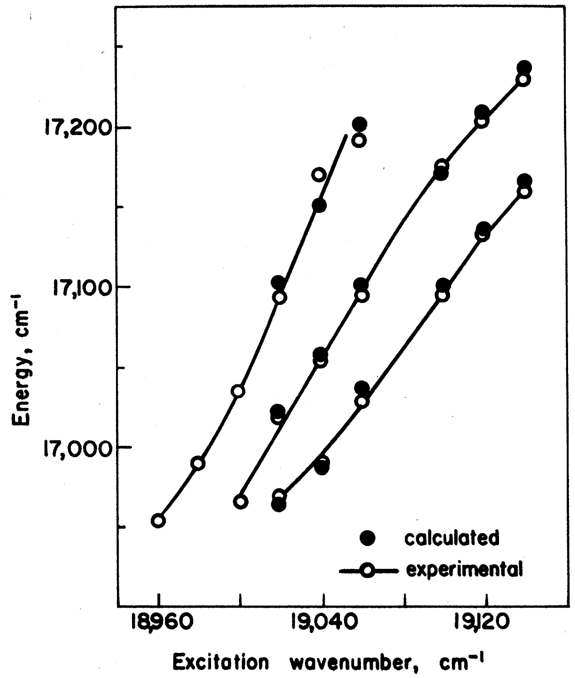

FIG. 4. Plot of the $^5D_0 \rightarrow {}^7F_1(\epsilon-)$ transition energies as a function of $^5D_1$ excitation energy. The solid circles indicate the $^5D_0 \rightarrow {}^7F_1(\epsilon-)$ energies calculated from the three $^5D_0 \rightarrow {}^7F_0$ lines observed in Fig. 1. The solid lines passing through the open circles represent the energies measured directly from the $^5D_0 \rightarrow {}^7F_1(\epsilon-)$ transition lines in Fig. 1.

gy. If we associate an increase in the energies of the $^5D_0$ and $^5D_1$ states with Eu ions in sites of greater distortion symmetry, then, by Ofelt's theory of transition probabilities for rare-earth ions,[9] electric-dipole transitions will increase in strength relative to magnetic-dipole transitions with increasing distortion. On this basis we would expect an increase in the $^5D_0$-$^7F_0$ luminescence intensity with respect to that of the $^5D_0 \rightarrow {}^7F_1$ luminescence as the excitation energy increases.

At the extreme high-energy side of the $^5D_1$ pump band, the laser should be resonant with ions only through their highest $^5D_1$ components, so that the spectra in Fig. 1 should reduce to a single-ion type having only one $^5D_0 \rightarrow {}^7F_0$ line. This is not observed. However, the relative intensities of the $^5D_0 \rightarrow {}^7F_0$ lines are a result of selection rules associated with both absorption to $^5D_1$ and decay from $^5D_0$, and the combination of these two factors may have the net effect that the luminescence becomes too weak to be observed when pumping only the highest-energy $^5D_1$ component. Cross relaxation could also have the effect of shifting the emission to lower frequencies, but the resulting inhomogeneous broadening would be greater.

A final point to be noted is that by pumping the $^5D_1$ state, many more sites are sampled than by pumping $^5D_0$ directly. In Fig. 1, $^5D_0 \rightarrow {}^7F_0$ transitions at energies as high as 17 450 cm^{-1} are easily seen even though the luminescence resulting from pumping $^5D_0$ directly above about 17 395 cm^{-1} is too weak to be observed.[5] This is not surprising, since the oscillator strength for excitation from $^7F_0$ to $^5D_1$ is much greater than to $^5D_0$.

In conclusion, we have shown that the problem of accidental degeneracies in the $^5D_1$ state of Eu in borate glass has been successfully resolved, and the technique of fluorescence line narrowing can yield the splittings within the excited state itself. By this technique, other states can be probed and further information obtained on the glass environment. In their crystal-field calculations, Brecher and Riseberg[1] utilized the splittings within the terminal J states to derive crystal-field parameters. In situations where there is no ground-state splitting, such as Gd^{3+}, or where it is obscured for some reason, the technique of using the splittings in the excited state may be the only means by which crystal-field calculations can usefully be performed. A necessary condition for this approach is that any ground-state splitting be large or that the homogeneous line broadening be small enough so as not to cause undue overlap in the luminescence and, hence, poor resolution. The Eu ion satisfies this condition easily, as seen from Fig. 1, where the $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_1$ lines do not overlap to any significant degree. This is especially true for Eu in oxide glasses, where the energy-level splittings are larger than, for example, in fluoride glasses.[10]

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