of sound near the λ line. In view of this, extrapolations to the λ line based upon the Pippard relations which ignore the temperature dependence of C_t and β_t would be quite risky. Rudnick and Shapiro[2] infer a velocity-of-sound discontinuity at the λ line based in part on such an extrapolation. We believe such an inference not to be justified and that the data can be explained by the temperature variation of C_t and β_t. In addition, if there is no velocity-of-sound discontinuity, then there would, of course, be no need to invent a new phase[4] for liquid helium.

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PREFERENTIAL EMISSION PHENOMENA IN THE AFTERGLOW OF X-IRRADIATED ALKALINE-EARTH FLUORIDES DOPED WITH RARE EARTHS*

J. Makovsky

Department of Physics, The Hebrew University, Jerusalem, Israel

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The trivalent rare-earth ions (RE^{3+}) enter the alkaline-earth fluorides (MeF_2, Me = Ca, Sr, Ba) lattices substitutionally at the divalent cation sites. Because of the variety of possibilities for charge-compensation mechanisms, the RE^{3+} experience in these lattices crystalline fields of differing strengths and symmetries. Upon excitation, the ions in the differently compensated sites produce characteristic spectra (site spectra). It is the simultaneous appearance of these site spectra that makes the optical spectrum of a RE^{3+}:MeF_2 a most complicated one.

The spectra of afterglows of x-irradiated RE:MeF_2 consist mostly of transitions characteristic of the RE^{3+}. High-resolution studies of such spectra show in our experiments that in certain circumstances the relative intensities of lines are different from the relative intensities observed during excitation and, furthermore, these relative intensities are time dependent. It is found that groups of lines exhibiting similar behavior with respect to these changes belong to certain site spectra.

This note deals with the afterglow spectra and their dependence on some parameters. We have studied these effects in detail for the system Gd^{3+}:CaF_2. The optical spectra of this system have been recently described[1] and the energy-level schemes of ions in eight different sites have been established. This analysis is the basis for the interpretation of the reported phenomena in the afterglow. Some of the implications of these phenomena will be pointed out.

The afterglow spectra of Gd^{3+}:CaF_2 were photographed between 2400 and 3400 Å using a Bausch & Lomb dual-grating spectograph with an effective resolution of 1 cm^{-1}. The excitation source was an x-ray (Machlet OEG-50) tube operated at 40 mA and 45-KV constant voltage. The samples were single crystals of different growth conditions and concentrations (10^{-3}-1 mole%). As a result of these variations their optical spectra consisted of different combinations of site spectra.[1]

In the afterglow spectra of Gd^{3+}:CaF_2 we observed transitions from the various Stark components of the ${}^6P_{7/2}$, the ${}^6P_{5/2}$, the ${}^6I$, and some of the ${}^6D$ levels. At low temperatures, as consistent with population considerations, the only transitions obtained are those from the low-lying Stark components of the various multiplets ($^6P,I,D$). The lines are usually sharp and their widths often instrumental (≤ 1 cm^{-1}).

Figure 1(a) is a spectrogram of the total radiation emitted in the warming process, 78 $\rightarrow$300°K, after the crystal had been x irradiated at 78°K. The ordinary optical spectrum of this crystal (fluorescence and absorption) consists of three site spectra: site C, identified as the cubic site, site A, the tetragonal F^--compensated site, and site B, which is presumably formed by two Gd^{3+} substituting for three Ca^{2+}.[1] As shown in this figure, this afterglow consists of all the sites originally present. If, on the other hand, the afterglow is studied at the same temperature at which the crystal is irradiated, only part of the site spectra usually appears. The composition of side spectra in an afterglow, thus obtained, is strongly temperature dependent and with a change in temperature can be drastically changed. At a given temperature the relative intensities of some lines change with the time. Groups of lines which do preserve their relative intensities, and so exhibit the same time dependence, were sorted out; each of these groups was found to belong to a specific site spectrum. Therefore, with suitable control of the two parameters—temperature and delay after the cessation of excitation—one is able to obtain preferentially the various site spectra. This is demonstrated in spectrograms (b), (c), and (d) of Fig. 1. These spectrograms were obtained at different temperatures which were in every case the same temperature at which the crystal had been x irradiated; the temperatures and delays after the cessation of excitation are indicated in the figure caption.

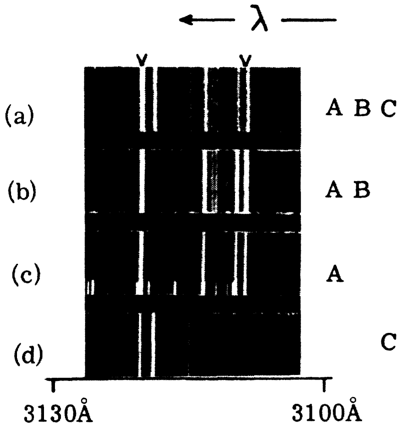

FIG. 1. The $^6P_{7/2} \rightarrow {}^8S_{7/2}$ transitions in some afterglows of an x-irradiated 0.05 mole% Gd:CaF$_2$. (a) Spectrum of the radiation emitted while the crystal is warmed from 78 to 300°K. The crystal had been x irradiated at 78°K (radiation dose $\sim 10^7$ R). All the site spectra originally present in the optical spectrum of the crystal appear here as well, viz., site spectra A, B, and C. The v marks in (a) indicate pairs of unresolved lines. (b), (c), and (d) are spectrograms of afterglows observed at the same temperature at which the crystals had been x irradiated. The delays T between the stop of excitation and beginning of exposure were controlled. To obtain these spectrograms, repeated exposures were needed; each exposure was of the order of 5 seconds. (b) Temperature about 15°C, $T = 1$ sec. Two site spectra appear, those of sites A and B. (c) Temperature about 50°C, $T = 1$ min. Here only the A site spectrum appears. (d) Temperature 78°C, $T = 5$ sec. The transitions are those of site-spectrum C.

The manner in which the intensities of the transitions $^6P_{7/2} \rightarrow {}^8S_{7/2}$ in site spectra A and B change with the time has been examined at room temperature. With both sites the decays were found to be exponential with decay times of 5 and 1.8 ± 0.3 minutes, respectively. The measurements were conducted over time ranges of about 20 and 5 minutes, respectively, starting 3 seconds after the cessation of excitation. We emphasize that in these experiments we studied well-resolved spectral components belonging to the different sites.

The phenomenon of preferential emissions in the afterglow of RE:MeF$_2$ and its dependence on the various parameters are consistent with a model of traps (for electrons or holes) localized at the vicinity of the RE ions. Of the various mechanisms conceivable as bringing about the observed afterglows, those involving temporary changes in the valency of the RE^{3+} ions into the divalent or tetravalent states seem the most probable. It is assumed that in the reconversion processes of the unstable RE^{2+} or RE^{4+} ions, produced in the irradiation, they relax to the RE^{3+} ground state with emissions characteristic of the RE^{3+}. These reconversions occur when electrons (or holes) trapped in the vicinity of the RE^{4+} (or RE^{2+}) are released by thermal agitation and recombine with charges of the opposite sign located at the adjacent RE ion. With a given host and RE ion the reconversion rate depends on the temperature and the specific site involved. Though it is premature to decide upon the physical nature of the traps to be associated with the various sites, it seems likely that the negative charge compensators, which apparently are not removed by the irradiation, are proper candidates for trapping of holes, and the interstitial positions in the vicinity of the RE ions are possible trapping centers for electrons.

The described above does not annul the possible existence of additional, unlocalized, trapping centers. These are probably of a special importance for RE ions in the cubic sites. In comparison with RE ions in other point-symmetry sites, RE ions in cubic sites are known to be exceptionally stable in the divalent state.[2] This is attributed to the absence of local charge compensators. A relatively great portion of the holes produced in the irradiation "corresponding" to the electrons captured by the RE^{3+} in the cubic sites are trapped somewhere far from these ions, and the recombinations which restore the ions to the trivalent state can take place only after such holes migrate to the vicinity of the RE ion.

In a recent publication,[3] Kiss and Staebler suggest that the thermoluminescence of RE: CaF_2 crystals consists of transitions characteristic of the RE^{3+} in the cubic sites. According to our experience [see for example Fig. 1(a)] this cannot be generally true. The discrepancy between Kiss and Staebler's observations and our own can probably be attributed to the special stability, just mentioned, of the RE^{2+} in the cubic sites. If a crystal is examined "long enough" after the cessation of excitation, it can happen that only ions in the cubic sites are left with a significant number in the converted divalent state.

It is hoped that studies of thermoluminescence glow curves and decay times at various temperatures, both applied to resolved components of the spectra, will shed more light upon these phenomena.

The reported phenomenon of preferential emissions in the afterglows, as shown here, is of considerable aid in the separation of the complicated optical spectra of RE^{3+}:MeF_2.[1] No doubt it can be applied in a similar manner to other spectra of ions in solids.

Studies of the effects reported are essential for understanding the mechanisms of excitation of optical emissions in solids with x rays[4,5] or other ionizing radiation. The delayed processes which bring about the emission of afterflow can be major contributors to the total intensities observed upon continuous excitation.[6] With some Pr^{3+}:CaF_2 samples these contributions amount to more than 50%.

It is of interest to test the possibility of preferential optical excitation of traps associated with the various sites. If this is indeed so, it will doubltlessly prove to be another powerful technique for separation of the various site spectra of RE^{3+}:MeF_2. Also, it will be a most interesting source for the much wanted experimental relationships between thermal activation and optical activation energies of trapped charged particles in ionic crystals.

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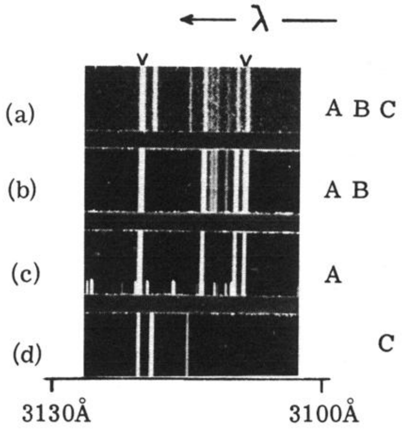

FIG. 1. The $^6P_{7/2} \rightarrow {}^8S_{7/2}$ transitions in some afterglows of an x-irradiated 0.05 mole% Gd:CaF$_2$. (a) Spectrum of the radiation emitted while the crystal is warmed from 78 to 300°K. The crystal had been x irradiated at 78°K (radiation dose $\sim 10^7$ R). All the site spectra originally present in the optical spectrum of the crystal appear here as well, viz., site spectra *A*, *B*, and *C*. The **v** marks in (a) indicate pairs of unresolved lines. (b), (c), and (d) are spectrograms of afterglows observed at the same temperature at which the crystals had been x irradiated. The delays *T* between the stop of excitation and beginning of exposure were controlled. To obtain these spectrograms, repeated exposures were needed; each exposure was of the order of 5 seconds. (b) Temperature about 15°C, $T = 1$ sec. Two site spectra appear, those of sites *A* and *B*. (c) Temperature about 50°C, $T = 1$ min. Here only the *A* site spectrum appears. (d) Temperature 78°C, $T = 5$ sec. The transitions are those of site-spectrum *C*.