edge the experimental assistance of R. Nielsen for the heat treatment experiments.

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EUROPIUM-TERMINATED CHROMIUM FLUORESCENCE IN $EuAlO_3$:Cr^{3+}

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An optical emission process is observed in which a Cr^{3+} ion, initially in the ^2E_g excited state, simultaneously emits a photon and excites a neighboring Eu^{3+} ion to an excited ^7F_J level. Transitions terminating on $J=1$ through 5 have been found.

In the optical-emission spectrum of Cr^{3+}-doped $EuAlO_3$ we observe, in addition to the two transitions from the crystal-field-split ^2E_g levels to $^4A_{2g}$ levels, a number of strong lines at longer wavelengths. The additional lines are not associated with the emission of single Cr^{3+}, Eu^{3+}, or other impurity ions, but consist of a compound process in which a Cr^{3+} ion makes a transition from the ^2E_g to $^4A_{2g}$ levels while a neighboring Eu^{3+} ion simultaneously goes to an excited state, and the energy difference is emitted as a photon. The effect is closely related to, but distinct from, the excitation of ion pairs observed by Varsanyi and Dieke.[1] It is quite different from the satellite lines observed in the spectrum of dark ruby, as there the level structure is determined not by single-ion levels, but by chromium-pair levels.[2]

The crystal has the orthorhombic crystal structure, $D_{2h}{}^{16}$-$Pbnm$, with four molecules in the unit cell.[3] There are two magnetically inequivalent rare-earth ion sites having C_{1h} (mirror plane) symmetry, and four inequivalent aluminum sites with C_i (inversion) symmetry. The Cr^{3+} substitutes for Al^{3+}, and the presence of a center of symmetry requires the transitions to be magnetic dipole.

Figure 1(a) shows the emission spectrum at 77°K in the immediate vicinity of the chromium R lines. Compare this with the emission from the isomorphic crystal $YAlO_3$:Cr^{3+}, Fig. 1(b), which shows the expected emission of two R lines and a very weak vibronic spectrum. The latter, when examined under higher gain, has a complex structure and shows no simple relation to Fig. 1(a). Thus the lines in Fig. 1(a) are not vibronics.

Paramagnetic-resonance measurements further indicate that Cr^{3+} is found only on the four inequivalent sites.[4]

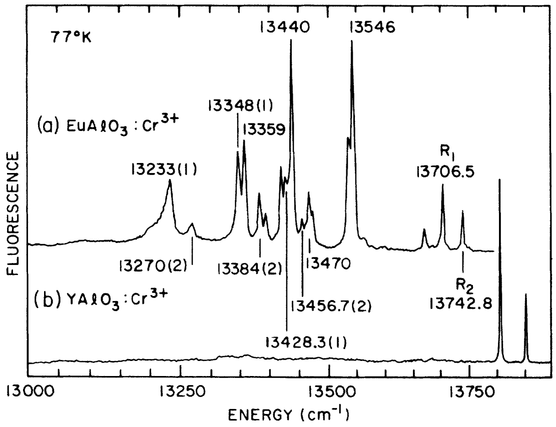

FIG. 1. (a) Emission spectrum of $EuAlO_3$:Cr^{3+} at 77°K. The temperature dependence of several of the satellite lines relative to the R_1 and R_2 lines is denoted by the bracketed 1 and 2, respectively. (b) R-line emission from $YAlO_3$:Cr^{3+} at 77°K.

The energy of the europium $^7F_1$ levels, which are split by the crystal field into three singly degenerate levels, was found by measuring the room-temperature absorption to the $^5D_0$ level in nominally pure $EuAlO_3$. The results are shown on the first line of Table I and essentially repeat the measurements made by Holmes et al. which are shown on the second line.[5]

Fluorescence measurements made at 4.2°K using $EuAlO_3$ gave the typical europium $^5D_0$ to ^7F_J emission[6] and confirmed the level assignments. A very weak spectrum identical to Fig. 1(a) indicated the presence of a minute amount of Cr^{3+} impurity. Measurements were made on crystals containing from 0.03 to 0.1% chromium. The intensity of the lines at 13 546 and 13 675 cm^{-1} did not vary linearly with the chromium concentration, while the remaining structure scales linearly with both the R line intensity and the doping level. Thus we attribute the former emission lines to either chromium pairs or rare-earth impurities, while the latter cannot have this origin.

Because of thermal depopulation of the upper ^2Eg level, the R_2 line is not seen at 4.2°K. In addition, only half of the lower-energy lines remain, allowing us to make the identification shown in the lower two rows of Table I. Three resolved lines are observed for the lowest energy $^7F_1$ level, and two for the middle level. The width of the 13 233-cm^{-1} line is comparable with the total width of the other lines and may contain a number of unresolved components. These may result from Cr^{3+}-Eu^{3+} pair interactions for which the levels of the inequivalent Eu^{3+} ions are displaced unequally by the introduction of the Cr^{3+} ion in the Al^{3+} site. Although the splitting of the $^7F_1$ levels is sensitive to low-symmetry distortions of the cubic field,[5] the line shift from multipole and exchange interactions between the ions may be appreciable.[7] For the particular lines chosen, the agreement with the $^7F_1$ levels is excellent, an indication that the sites responsible for these lines are well removed from the Cr^{3+} sites. At the larger separation, the weaker coupling is partially compensated for by the increase in the number of Eu^{3+} sites.

Table I. Energies (in cm^{-1}) of the $^7F_1$ Eu^{3+} levels as determined from the pure $EuAlO_3$ absorption and the Eu^{3+}-assisted Cr^{3+} fluorescence. In the site coordinate frame, the $^7F_1$ wave functions transform as x, y, and z, and the energies are labeled by this convention.

		E_y	E_z	E_x
$EuAlO_3$[a]		280	358	471
$EuAlO_3$[b]		281	359	479
$EuAlO_3:Cr^{3+}$	$R1$	278.2	358.5	473.5
$EuAlO_3:Cr^{3+}$	$R2$	286.1	358.8	472.8

[a] Present measurement.

[b] Results of Holmes, Sherwood, Van Uitert, and Hufner (Ref. 5).

Transitions terminating on the $^7F_2$ level are shown in Fig. 2. The crystal field splits the $^7F_2$ into five components, and the energy of these levels in $EuAlO_3$ is shown in the top of Fig. 2. The 1064.4-cm^{-1} europium line is apparently spurious; it was not observed by Holmes et al.[5] The agreement with remaining lines is excellent; note, in particular, the shoulder on the line at 12 700 cm^{-1} corresponding to the 1001.6-cm^{-1} line.

At 4.2°K, seven lines are observed between 8400 and 8600 Å, and these are identified as the emission terminating on the $^7F_3$ level. Transitions terminating on the $^7F_4$ level are found between 9100 and 9500 Å. Above 10 100 Å a number of lines are observed which are attributed to transitions terminating on the $^7F_5$ level. Taking the maximum intensity of the $^7F_1$ terminated line as unity, the peak intensities of ^7F_J for $J=2$, 3, 4, and 5 are, respectively, 0.04, 0.28, 0.15, and 0.09. The values have been corrected for changes in the spectral response of the S-1 photomultiplier tube.

Fluorescent-lifetime measurements were made using a short-duration flash ($\sim 3\times10^{-6}$-sec) and monitoring the fluorescence decay on an oscilloscope. To within the experimental accuracy, the lifetimes of the Cr^{3+}-doped crystals were unchanged on decreasing the temperature from 77 to 4.2°K. For $YAlO_3:Cr^{3+}$ we find $\tau=(53\pm1)\times10^{-3}$ sec which is slightly longer than $\tau\approx10^{-2}$ sec obtained by Imbusch for the magnetic dipole lines in $MgO:Cr^{3+}$.[8] At 77°K the sum of the R-line intensities is 20% of the total intensity. The R-line lifetime thus is 0.26 sec. Using $f\tau=1.6\times10^{-9}$ sec with the calculated value of the magnetic-dipole R-line oscillator strength of $f=5.5\times10^{-9}$, we find $\tau=0.35$ sec. This indicates the R lines are magnetic dipole with a quantum efficiency of 72%.

The 4.2°K emission of $EuAlO_3$ initially decayed with $\tau\approx2.5\times10^{-5}$ sec. This was followed by a decay having a time constant of 10^{-3} sec.

In $EuAlO_3:Cr^{3+}$ the emission from the R lines and the satellites decayed exponentially with

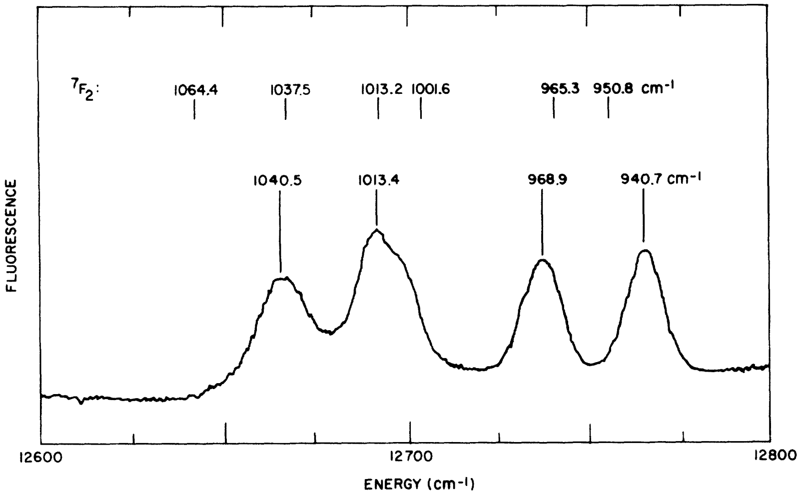

FIG. 2. Chromium emission terminating on the $^7F_2$ europium levels at 4.2°K. The separation from R_1 is given above each line. Shown on top is the $^7F_2$-$^7F_0$ level separation obtained from pure $EuAlO_3$ fluorescence.

$\tau = 10^{-5}$ sec. This is two orders of magnitude shorter than the 4×10^{-3}-sec lifetime in ruby, where, because of a lack of inversion symmetry, the lines have electric-dipole polarization.[9] At 4.2°K it is estimated that less than 2% of the total emission is in the R_1 line. Measurements made using doped $YAlO_3$ and $EuAlO_3$ crystals under identical experimental conditions indicate the total radiative efficiencies are equal to within a factor ±2. The main uncertainty results from unknown variations of the chromium doping levels and the possibility of energy transfer between the Eu^{3+} and Cr^{3+} ions. This rules out the possibility that the short lifetime results from a rapid nonradiative decay. Well over 70% of the total emission terminates on the $^7F_1$ level. The weak intensity of the remaining lines results from admixing of the J levels by the crystal field; in particular, the rhombic field accounts for the large $^7F_3$ intensity.

Using the measured value of the lifetime, we compute the total oscillator strength to be 1.6×10^{-4}. The strong line at 13 440 cm^{-1} contains about 8% of the total emission, and we assume this line to result from interactions with eight nearest-neighbor europium ions. Then $f = 1.6\times10^{-6}$ for a single Cr^{3+}-Eu^{3+} pair. The oscillator strength may be estimated from

$$f = f_0(|\mathcal{H}|/\Delta E)^2,$$

where $\mathcal{H}$ is the perturbation coupling the ions via the higher energy excited states, f_0 is the oscillator strength to these levels, and ΔE is their energy separation. Using reasonable values for the energy shift $\delta E \approx |\mathcal{H}|^2/\Delta E$ of about 1 cm^{-1} per pair, $f_0 \approx 10^{-1}$, and $\Delta E \sim 10^5$ cm^{-1} yields $f \approx 10^{-6}$ in good agreement with the previous calculation. A more complete description of the experimental results and an explanation of the Cr^{3+}-Eu^{3+} coupling via exchange will be reserved for a future publication.

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