Interpretation of europium(III) spectra

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The trivalent europium ion (Eu^{3+}) can exhibit an intense red photoluminescence upon irradiation with UV radiation. This property is exploited in red-emitting lamp phosphors such as $Y_2O_3:Eu^{3+}$. However, Eu^{3+} is also of interest from a theoretical point of view. There are several reasons why the Eu^{3+} ion is so often used as a spectroscopic probe for the symmetry of first coordination sphere of a trivalent lanthanide ion. First of all, the ground state ($^7F_0$) and the most important emitting excited state ($^5D_0$) are non-degenerate and are thus not split by the crystal-field effect. This greatly facilitates the interpretation of the experimental absorption and luminescence spectra. Second, the most important transitions in the luminescence spectra are from the $^5D_0$ excited state to ^7F_J levels with a low J value (J = 0, 1, 2). This also facilitates the interpretation of the spectra, because the number of possible crystal-field transitions is small. Third, the wave functions of the ^7F_J levels and of the $^5D_0$, $^5D_1$ and $^5D_2$ excited states are well described within the intermediate coupling scheme and J is a good quantum number. J-mixing is limited so that there is only a small relaxation of the selection rules and an accurate theoretical description of the energy level structure of the $4f^6$ configuration of Eu^{3+} is possible. Fourth, the different $^5D_0 \rightarrow {}^7F_J$ lines are well separated, so that there is virtually no overlap between the crystal-field levels belonging to different ^7F_J levels. Fifth, europium(III) compounds often show an intense luminescence due to the large energy gap between the $^5D_0$ excited state and the highest level of the ^7F_J manifold. It is also convenient that the luminescence is in the visible spectral region (red luminescence). Sixth, the Eu^{3+} ion shows only a weak vibronic coupling and as a consequence the crystal-field transitions are narrow, even at room temperature. The crystal-field fine structure is relatively easy to resolve, although spectral overlap may occur in case of weak crystal-field effects. This lecture gives an overview of the spectroscopic properties of Eu^{3+}. The different transitions in the luminescence spectra of europium(III) compounds are discussed in detail. It will be shown to what an extent the Eu^{3+} ion can be used a probe for the local symmetry of the lanthanide ion in crystalline host matrices.