Relation between Eu^{2+} and Ce^{3+} f$\rightarrow$d transition energies in inorganic compounds

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A relationship between the Eu^{2+} and Ce^{3+} f$\rightarrow$d transition energies in inorganic compounds was noticed already in 1984 by van Uitert [1]. At present, much more data on the energy of the first *fd* transition in Ce^{3+} is available [2]. The same applies to Eu^{2+} [3], and the relationship can be studied in more detail.

In this work information has been selected on those compounds where the *fd* transition energy is known for Ce^{3+} as well as for Eu^{2+} at the same site in the same compound. The data is shown in Fig. 1 where the transition energy in both lanthanides is displayed against the transition energy in Ce^{3+}. In addition to *fd* absorption data, also *df* emission data has been used. Because Eu^{2+} does not emit on trivalent cation sites all information pertain to divalent sites in compounds [3]. The data on Eu^{2+} scatter around a straight line given by

$$E_{Eu} = 0.64 E_{Ce} + 4300\,\mathrm{cm^{-1}} \qquad (1).$$

This implies that once the transition energy of Ce^{3+} is known in a compound, that of Eu^{2+} if at the same site in the same compound can be roughly estimated. The same can be done for Ce^{3+} once information is available on Eu^{2+}.

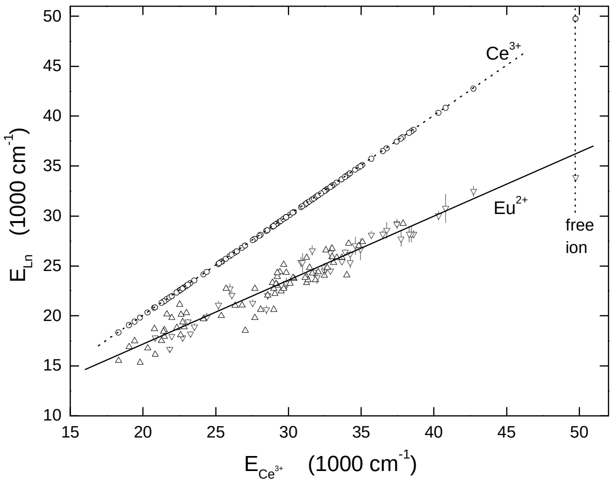

Figure 1 The energy of the $f\leftrightarrow d$ transitions in Eu^{2+}and Ce^{3+}. Δ, *fd* absorption transition in Eu^{2+}. ∇, *df* emission transition in Eu^{2+}. o, $f\leftrightarrow d$ transitions in Ce^{3+}.

The energy of the *fd* or the *df* transition depends on 1) the crystal field splitting ε_{cfs} of the 5d configuration, 2) the centroid shift ε_c of the 5d configuration, and 3) the Stokes shift ΔS between absorption and emission [4]. Since a proportional relationship as in Eq. (1) exists, a proportional relationship should also exist for ε_{cfs}, ε_c and ΔS.

Crystal field splitting and centroid shift is known for many different Ce^{3+} doped compounds, see [4] and references therein. For Eu^{2+} a fair estimate has been made on compounds providing sites of O_h symmetry. It appears that the Stokes shift and the crystal field splitting in Eu^{2+} is 0.61 and 0.77 times the value for Ce^{3+}, respectively. The centroid shift appears 0.61 times that of Ce^{3+}. However there are indications that this value scales with the ionicity of the compounds, and it seems smaller in fluorides.

The fact that the ratio's between Stokes shift, centroid shift, and crystal field splitting are slightly different from the ratio of 0.64 in Eq. (1) explains part of the data scatter around the line drawn in Fig. 1. Another part stems from the presence of a charge compensating center whenever Ce^{3+} occupies a divalent cation site.

The results from this work help in predicting spectroscopic properties of divalent lanthanides once that of trivalent lanthanides is known, and vice versa. The found relationship may also be used to signal erroneous data or to provide clues to the nature of charge compensating defects and lattice relaxation.

References

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