Mixed Eu^{2+} - Eu^{3+} valence state in Eu- and Na-doped PbSe

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The Eu atoms in $Pb_{1-x}Eu_xSe$ have long been assumed to be divalent. We show that p-type doping of this semiconductor with Na can modify the Eu valence: a mixed, Eu^{2+} - Eu^{3+} state appears in $Pb_{1-x-y}Eu_xNa_ySe$. Magnetization, carrier concentration, resistivity, and thermopower of $Pb_{1-x-y}Eu_xNa_ySe$ are reported for a number of samples with different x and y. An increase in thermopower at a given carrier concentration was identified and attributed to the presence of enhanced ionized impurity scattering. A strong decrease in the hole concentration is observed in $Pb_{1-y}Na_ySe$ when Eu is added to the system, which we attribute to a Eu^{2+} – Eu^{3+} self-ionization process. This is evidenced by magnetization measurements, which reveal a significant reduction of the magnetic moment of $Pb_{1-x}Eu_xSe$ upon alloying with Na. The conclusions are supported further by the electronic structure calculations, which show an instability of the $4f^7$ configuration of the Eu^{2+} ion appears with Na doping.