

# Fe donor in ZnO: a Half-resonant Character Driven by Strong Intracenter Coulomb Coupling

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Typically, a donor introduced to a semiconductor induces an energy level within the band gap, which is close to the bottom of the conduction band. Some donors are, however, resonant, which means that their donor (0/+) ionization level is situated within the conduction band. As a consequence they autoionize spontaneously even at zero temperature.

According to our first principles calculations, iron dopant in ZnO presents a particular case of a half-resonant donor representing an intermediate situation: Fe<sup>2+</sup> charge state is unstable because the donor level of Fe<sup>2+</sup> is within the conduction band continuum, but the autoionization from 2+ to 3+ charge state is only partial because the donor level of the ionized Fe<sup>3+</sup> is below the bottom of the conduction band. A complete ionization of the Fe would require a non-zero ionization energy of around 0.1-0.2 eV. We find that large, about 1 eV, difference in the donor level energies of the 3+ and 2+ charge states is a consequence of a large intrashell Coulomb coupling between *d*(Fe) electrons.

We confirm the results of theoretical considerations by studies of polycrystalline (Zn,Fe)O films with the Fe content attaining 0.2% using several experimental methods like electron paramagnetic resonance, magnetometry, conductivity, excitonic magnetic circular dichroism (MCD) and magneto-photoluminescence (PL).

The samples are *n*-type, with the room temperature electron concentration increasing from about  $5.4 \cdot 10^{15} \text{ cm}^{-3}$  to  $1.5 \cdot 10^{16} \text{ cm}^{-3}$  upon doping with 0.2% of Fe. The donor character of the Fe ions and activation energy of conductivity of 0.14 eV remain in agreement with the theoretical estimations. Relatively low electron concentrations indicate a high degree of compensation of Fe donors, most possibly by the zinc vacancies. The presence of compensating acceptors is also reflected by the DAP recombination observed in the PL.

Brillouin-like dependencies found in measurements of MCD and of PL in magnetic field along with a clear Curie-paramagnetic dependence on temperature of magnetization determined from magnetospectroscopy confirm presence of Fe ions in 3+ valency and the ion-carrier *s,p-d* exchange interaction in the (Zn,Fe)O.

The presented results help explaining the fact that despite transition metal ions in II-VI semiconductors exhibit typically a native 2+ valency, for the case of ZnO 3+ or mixed 3+/2+ valency was previously reported.