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Separation of one- and many-electron effects in the excitation spectra
of 3d impurities in semiconductors

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We present a new multiplet theory that separates mean-field from multiplet effects in the excitation and donor-acceptor ionization spectra of localized impurities. Analysis of the experimental data for all 3d im-purities in Zno, ZnS, ZnSe, and Gap for which sufficient data exist and for the bulk Mott insulators CoO, MnO, and NiO reveals, for the first time, regular chemical trends in many-electron effects with the impuri-ty and the host-crystal covalency and

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Co. In the classical crystal-field approach of Sugano,
Tanabe and Kamimura 2 9 differential hybridization is ig-
nored (hence X, =A.

,), and all e~ and I" orbitals are as-
sumed to be equally deformed in the anisotropic field (same

A for ail e™I"),and hence A is artificially dropped from the
model. Pitting the impurity spectra produces 8, C, and ACF.
In the Hemstreet-Dimmock (HD) approach, 7

it is assumed

that a MF calculation for a specified configuration e I" in-
cludes

e

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one, showing a minimum at Mn and maximum for the
heavier 3d impurities, as found in recent calculations, 5 6

an

increase in b.eff with covalency (GaP vs II-VI compounds),
and a decrease with lattice parameter. Our fits are as good, and usually better than those obtained previously in the
standard approach2 8 9

(e.g.,

in CoO, where the number of
observed transitions exceeds the number of parameters, our
method predicts the four unfitted transitions to within 0.02
eV). Previous discrepancies between calculations on bulk
oxides and the conventional crystal-fieM fitted parameters
are removed (e.g.,

in NiO, b.cF= 1.13 eV, and the calculated

MF value~ b,,rr=0.72 eV. Our result is A,rq=0. 75 eV).
The orbital deformation parameters [Figs. 1(b) and 1(c)]
decrease rapidly with covalency, but are nevertheless

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tronic structure calculations (i.e., with no multiplet effects).
%e see that the large deformation parameters for Mn deter-
mined optically [Figs. 1(b) and 1(c)], combined with its
high spin, produce

produce