TRANSITION METAL IMPURITIES IN SEMICONDUCTORS

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Abstract

First-principles self-consistent Green's function methods are used to understand the apparent dichotomy between the atomically-localized and covalently-delocalized characteristics of 3d impurities in semiconductors, and to unravel intriguing chemical trends and universalities.

1. DUALITY OF 3d IMPURITIES: LOCALIZED AND EXTENDED CHARACTERISTICS

Despite extensive experimental studies over the past 30 years (reviewed recently in Ref. 1), the electronic structure of 3d impurities in semiconductors has received theoretical attention only rather recently. Rapid progress has, however, been made in this area, through use of a wide range of theoretical techniques, including cluster models[2], continued-fraction Extended Hückel methods[3], empirical tight-binding models[4], Anderson-type model Hamiltonians[5], and more recently, by first-principles, self-consistent Green's function models[6-10] utilizing the local density formalism. This system has attracted my attention not only because of its obvious importance in technological device issues (e.g., solar cells, semi-insulating substrates, LED's, lifetime-controlling dopants, etc.), but primarily due to an intriguing **duality** that the experimental data on these impurities seem to exhibit. The intellectual tools established since Van-Vleck and Bethe considered the structure of 3d atoms in non spherical chemical environment have prepared one to think about impurities as exhibiting **either** atomically-localized characteristics (as is the case for 3d atoms in ionic coordination compounds), **or** covalently-bonded, "extended" characteristics (as is the case for shallow, "hydrogenic" impurities). This dichotomy is rooted in

numerous text books and review articles and constitutes the working
paradigm in impurity physics. Examination of the experimental data
for 3d impurities in semiconductors[1] suggested to me, however, that
depending on which experimental probe is looked at, **both points of
view are valid at the same time.** This can be appreciated as
follows. Consider the observed free-ion and impurity ionization
energies (donors and acceptors) depicted in Fig. 1, the observed
hyperfine coupling constants shown in Fig. 2, the observed g-values of
Table I, and the absorption spectra of Fig. 3.

Arguing for the covalently-delocalized model of such impurities,
I note the following:

(A) The **rate** at which impurity ionization energies change with atomic
number (Fig. 1 b-f) is ~ 10 times smaller than in free-ions (Fig. 1a),
suggesting bond-formation and chemical interactions in the solid.
(B) The Mott-Hubbard Coulomb repulsion energy for impurities [i.e.,
the difference between two consecutive ionization energies such as
$E(0/+) - E(0/-)$] is ~ 50-100 times smaller than for free-ions, sug-
gesting strong (and nonlinear) screening in the solid. (C) The **abso-
lute** impurity ionization potential (e.g., the difference between the
host work function and the impurity energy of Fig. 1b-f taken with
respect to the valence band maximum] is about 5-7 eV in all systems
(Fig. 6 below), exactly as the redox potential (relative to vacuum
too) of such ions in **strongly polarizeable media,** (e.g., water), or
even for Fe in Heme proteins[1], suggesting again strong polarization
and interactions with the host crystal. (D) The hyperfine-coupling
constants in semiconductors (Fig. 2 and Table I) are reduced
dramatically relative to free-ions or to 3d impurities in ionic
compounds, suggesting strong covalency. (E) The angular momentum part
of the g-values (Table I) are quenched, and the spin-orbit
splittings[1] are reduced, both suggesting once more covalency.
(F) The Mössbauer Isomer shifts (e.g.[1], Fe in Si and III-V's) seems
not to depend much on the formal oxidation state, suggesting that the
host crystal resupplies the impurity with s electrons when ionized,
again a manifestation of impurity-host interactions.

Arguing for the opposite point of view, namely that 3d impurities
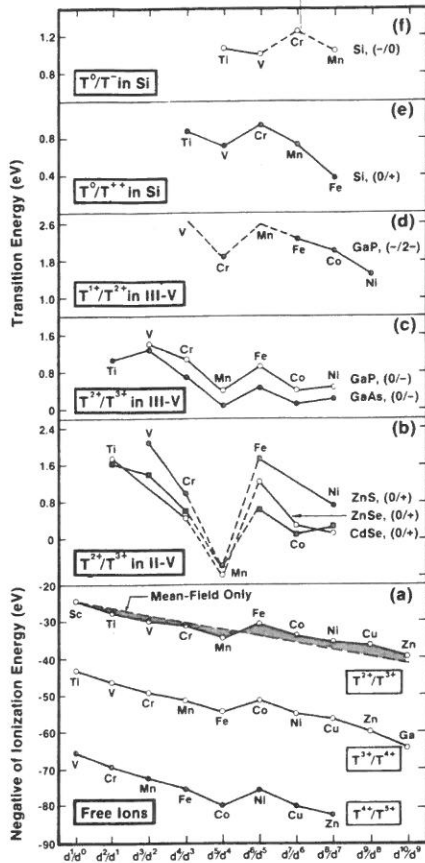in semiconductors are "localized", I note the following:

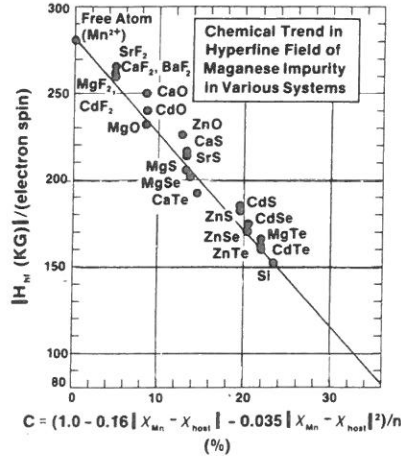Fig. 1: Observed[1] donor and acceptor (b-f) and free-ion (a) ionization energies of 3d ions.

Fig. 2: Trends in the observed[1] hyperfine field $\underline{vs}$ the phenomenological electronegativity C, for Mn.
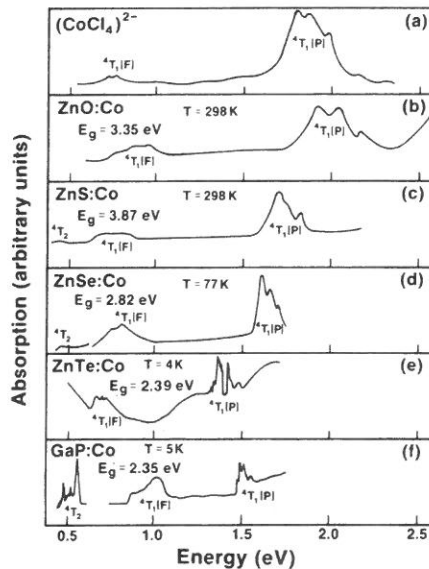

Fig. 3. Absorption spectra[1] of Co in different media. $\longrightarrow$

Table I: Calculated and observed[1] g-values and hyperfine coupling constants A (10^{-4} cm^{-1}) for impurities in Si.

Impurity	g_{calc}	g_{exp}	A_{calc}	A_{exp}
Ti$^+$, J=3/2	1.9912	1.9986	+4.7	±5.2
Cr$^+$, J=5/2	1.9986	1.9978	+11.0	+10.7
Cr^0, J=2	3.0828	2.97	+14.0	±15.9
Fe^0, J=1	2.0430	2.0104	-5.2	±6.9
Fe$^+$, 3=1/2	3.5582	3.524	-3.9	±3.0

(I) the atomiclike multiplet structure (indicative of localized states) is largely retained in the solid (Fig. 3), with similar ranges of d→d* excitation energies as in free-ions; (II) the existence of

atomiclike high-spin (Hund's rule) ground states (Fig. 1.), suggesting that as large as crystal-field effects may be, exchange effects (increasing with localization) usually outweigh them; (III) the existence of only small (or vanishing) Jahn-Teller energies suggests the dominance of localization-induced exchange interactions over symmetry-lowering elastic deformation; (IV) the appearance of most of the ENDOR spin density near the impurity site suggests that, at least inside the central cell, the spin density is atomically localized; (V) the occurrence of a strong half-shell d^5/d^4 stabilization (see local minimum in Fig. 1b-f) like that in the **free** 3d ions (Fig. 1a) suggests that much of the atomic characteristics are preserved in the solid; and, (VI) the great similarity between d→d* excitation energies of 3d impurities in zincblende and wurtzite II-VI semiconductors (which differ in their coordination structure only beyond the second shell of neighbors) suggests that the impurity wavefunctions may be localized.

Our theoretical work in this field had convinced me that the only correct way to think about these systems is to describe them as **atomically-localized and covalently-delocalized at the same time**; a duality not unlike the classical vs the quantal (DeBroglie's) view on light. I describe a few illustrations of this in the next section, were results of Green's function calculations are given.

2. THE NATURE OF THE DUALITY

When a 3d atom is introduced into a wide-band-gap narrow-valence-band **ionic material**, its d orbital energies fall naturally inside the band gap region. The 3d system is then only weakly coupled to the host crystal, in the sense that (external) perturbations exerted on this ion (e.g., ionization, external fields, etc.) must be absorbed by the ion itself. In contrast, we find that a 3d impurity in a **semiconductor** distributes most of its orbital character as broad hybridized resonances within the (wide) valence band, and only a faint shadow of it is captured inside the (narrow) band gap region. This is illustrated in Fig. 4, showing that most of the effective charge (Q) and local magnetic moment (μ) is contributed by the valence band resonances (VBR). Symmetry, however, disallows any coupling between the e-type (or Γ_{12}) 3d orbitals (which, in substitutional tetrahedral symmetry point to the **next** nearest neighbors) and the nearest ligand
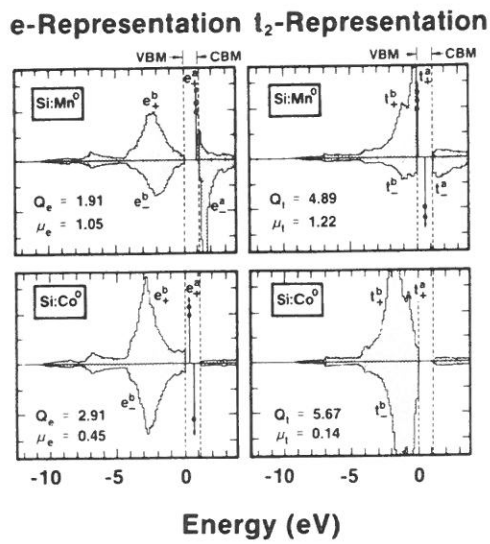
e-Representation t₂-Representation

Fig. 4: Calculated local density of states for impurities in Si.
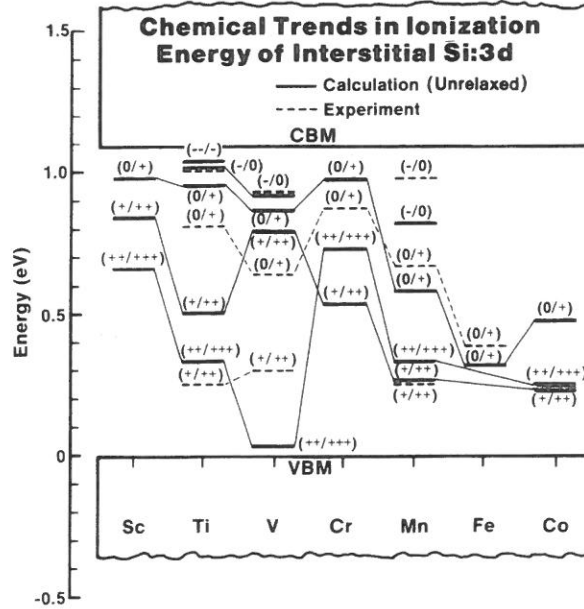
Fig. 5: Calculated and observed[1] impurity ionization energies in Si.

atoms. These e orbitals hence remain localized, whether they resonate in the valence band (heavy 3d impurities) or are in the band gap (light 3d impurities). This simple picture, emerging from our studies[6-9] on 3d impurities in Si, III-V's and II-VI's contains the essential physics of the coexistence between localized and delocalized characteristics. This situation has a number of significant physical implications. When a gap level is ionized in an absorption or thermal experiment, reducing thereby the charge around the impurity atom, the valence band resonance wavefunctions respond by becoming more localized around the impurity[6], returning thereby much of the charge lost by the gap level. The **effective** charge around the impurity atom in a semiconductor hence remains nearly constant in different ionization states, explaining the observed constancy of the Mössbauer isomer shift (point F). This "self regulating response"[6] (analogous to Homoestasis in biological systems) explains also why so many different charge states can exist in a narrow (band gap) energy range (Fig. 1b-f) as manifested by a small Mott-Hubbard Coulomb energy (point B). It is important, however, to note that only direct Coulomb interactions are screened effectively by this self-regulating response: whereas the band gap levels and the valence band levels have opposing (hence, compensating) contributions to the **impurity**

charge, both types of levels contribute in the same direction to the **local magnetic moment**; exchange interactions are hence affected far less by this screening. The different responses of Coulomb and exchange interactions to screening underlines the phenomena of exchange-induced negative "effective U"[8], whereby the (largely unscreened) exchange **attraction** overwhelms the (strongly screened) Coulomb **repulsion**. This idea is yet to be tested experimentally. This result predicts also that **spin**-densities (as observed by ENDOR) would be mostly "localized" in the central cell (point IV) and will change with ionization far more than the impurity site **charge** density (as observed by Mössbauer measurements). Furthermore, it suggests that the main change in charge densities with ionization would occur on the **ligands** (where much of the amplitude of the VBR exists) rather than on the the **impurity**.

The occurrence of hybridized valence band resonances is also largely responsible for the covalent quenching of the angular momentum part of the g-value (Table I), and the spin-orbit splitting (point E), the reduction in the hyperfine coupling constants (point D and Table I) the attenuation of the rate of change of ionization energies along the 3d series (point A), and for the overall reduction in the magnitude of the ionization energies relative to free-ions (point C). The substantial coupling of the impurity to its ligands through the valence band resonances is manifested also by atomic relaxation effects: direct calculations[7] of the force exerted by the impurity on its ligands has shown for interstitial impurities in Si that the first ligand shell (containing 4 atoms) moves **outwards**, whereas the second ligand shell (containing 6 atoms) moves **inwards**. This results in an effective ~**10-fold coordinated 3d atom**, a rare situation in 3d coordination chemistry, but nevertheless one exhibited by numerous bulk 3d silicides.[7] This coupling is so pronounced that it would seem that the correct chemical picture of the system should involve a "complex" of the impurity with its 10 ligand neighbors, viewed as a "local silicide".

In contrast with the strong Coulomb screening and hybridization, the weak screening of exchange interactions is responsible for the survival of atomiclike high-spin (Hund's rule) ground states

(point II) and the characteristic break in the trends of the ionization energies at the d^5/d^4 "Hund's point" seen in Fig. 1 (Point D). Combined with the symmetry and angular momentum imposed localization of the e-type 3d orbitals, these two effects are responsible also for the existence of atomiclike multiplet effects (point I) and for the overall signature of localized 3d orbitals (points III and VI).

3. TRENDS IN IONIZATION ENERGIES

While the calculated[6-8] donor and acceptor energies agree rather well with experiments (e.g., see Fig. 5 for interstitial impurities in Si), they do give the impression of an absence of recognizable and simple chemical trends. Caldas et al.[19] have observed, however, that if one

Fig. 6: Universality of VRBE of 3d impurities in various hosts.

refers these energies to an intrinsic reference energy characteristic of the host (e.g., the vacuum level), **these "vacuum referred binding energies" (VRBE) are approximately constant for the same impurity in different host crystals** (Fig. 6). This rule can therefore be used to predict the binding energy of an impurity in a host AC if the value in another crystal, BC, is known[11]. Conversely, I showed[9] that the knowledge of the impurity level both in AC and in BC (or in their alloy) can be used to deduce the intrinsic valence band offset between the two semiconductors, thereby providing complementary information to that deduced by photoemission from interfaces, (essential in understanding Schottky barriers too).
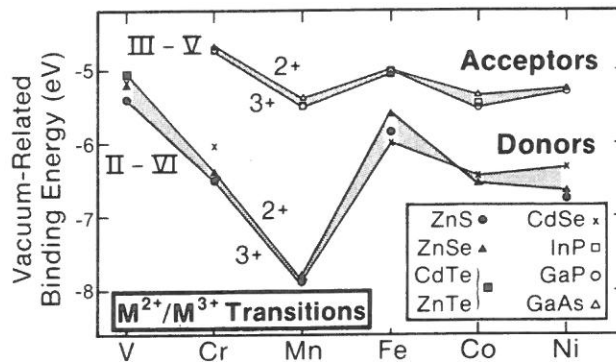
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