CHEMICAL TRENDS AND UNIVERSALITIES IN THE SPECTRA OF TRANSITION METAL IMPURITIES IN SEMICONDUCTORS

M. Caldas[+], A. Fazzio[§] and Alex Zunger

Solar Energy Research Institute, Golden, Colorado 80401 USA

Abstract

Deconvolution of the excitation spectra of the 3d impurities in ZnS, ZnSe, GaAs, InP and GaP into a one-electron mean-field part and a many-electron multiplet correction, reveals chemical regularities as well as universal (i.e., host independent) trends. It also suggests the possibility of occurrence of a negative effective-U, likely to arrear in GaAs:Mn.

I. Introduction

In this work we present a simple procedure (1) that can be used to separate, for localized impurity states, the observed acceptor energy $E_A(0/-)$, donor energy $E_D(0/+)$, the effective "Hubbard U" i.e. $U \equiv E_A(0/-) - E_D(+/0)$, and the intra-center excitation energies ΔE_{ij} between multiplets i and j, into: (i) a part due to mean-field (MF) contributions, (describable in principle by restricted electronic structure calculations), and (ii) a multiplet correction (MC) part due to many-electron effects. The method differs in a number of ways from other multiplet approaches (2-4). The deconvolution of the data into MF effects and MC allows us to (i) inspect the chemical trends in the many-electron effects in different host crystals (ZnS, ZnSe, GaP, InP, GaAs) and impurities (the 3d series studied here), (ii) identify the piece (i.e. MF, not MF+MC) of the experimental energies that contemporary mean-field electronic structure calculations should legitimately reproduce, (iii) predict hitherto unobserved transitions, and (iv) speculate on the possibility of a different type of "effective negative U" (likely to occur in GaAs:Mn) where the negative multiplet correction to U plays the dominant role in outweighing the positive electronic piece of U, even if lattice distortions are insufficient to produce a Anderson negative U.

II. Methodology

We outline briefly this approach (1). It assumes, following Slater (5), that the total energy $E_{tot}(m,n)$ calculated with MF theory for a system of

fixed configuration (say, $e^m t_2^n$) contains the average energy $\hat{E}_{m,n}(A,B,C)$ of all single-configuration energies that evolve from (m,n). Here, A is the totally symmetric interelectronic repulsion, and B,C are the anisotropic Racah parameters. The true many-electron energy for a given mutliplet i also includes a spin- and symmetry-dependent correction $\Delta E^{(i)}_{m,n;m',n'}(B,C)$, due to interactions within a single configuration, and the configuration mixing. The effective crystal-field splitting $\Delta_{eff}(m,n;m',n')$ is identified as the difference $E_{tot}(m,n)-E_{tot}(m'n')$ in the mean field total energies that separates the two configurations. It includes therefore both the classical configuration-independent [Tanabe-Sugano, (2)] "crystal field splitting" Δ_{CF}, as well as MF screening effects, plus a term due to differences in average multiplet energies in the two configurations. Applying the classical multiplet theory (6) within this separation of variables [hence, the nonuniqueness in the local density decomposition (7) does not appear], we are able to show that all of the problematic (2-4) configuration dependence of A(m,n) can be renormalized into Δ_{eff}, and that the multiplet corrections do not depend on A. The transformed problem results in a set of matrix equations, different from those currently in use (2)-(4), that incorporate explicitly the separation of average MF effects from multiplet corrections.

This general formalism can be applied in two ways. First, one could compute from MF wavefunctions all of the symmetry and spin-dependent anisotropic many-electron integrals underlying $\Delta E^{(i)}_{m,n;m',n'}(B,C)$ as well as the MF energy separations $\Delta_{eff}(m,n,;m',n')$, and insert them into the general matrix equations (1) to obtain the multiplet spectra and their MF vs MC components. Alternatively, one may wish to establish the magnitude and trends in the multiplet corrections underlying the experimental data itself, using the integrals of the theory as internal parameters. In view of the scarcity of data, we reduce the number of independent integrals (4) by characterizing all occupied impurity-induced e and t_2 orbitals by the orbital deformation parameters λ_e and λ_t, [as in ref. (4), different from those in Ref. (3)] measuring the ratio of the interelectronic interactions in the solid to those in the free ion [characterized by (6) B_o and C_o]. Further, since only a few d→d* absorption lines are usually detected, we replace $\Delta_{eff}(m,n;m',n')$ by a single value. The observed d→d* transitions for the 2+ oxidation state are then used to determine λ_e, λ_t and Δ_{eff} for all 3d impurities in ZnS, ZnSe, InP, GaAs, and GaP for which reliable data exists. When the number of observed transition energies is small, we calculate ranges in these parameters consistent with the data.

The intra d excitation energies ΔE_{ij} contain a mean field part (Δ_{eff}), as well as a MC, displayed as the shaded area in Fig. 1a. Using λ_e, λ_t and Δ_{eff} we can calculate the multiplet correction for the ground state total energy of the 2+ ions (A^o in II-VI's, A^- in III-V's), given in Figure 1b. If we neglect the small variation of λ_e,λ_t with oxidation state, we can repeat the calculations for the 3+ ions (A^+ in II-VI's, A^o in III-V's), obtaining the multiplet corrections for their ground states. The difference in MC's for the ground states of the 3+ and 2+ ions is the MC for donor transition energies in II-VI's and the acceptor transition energies in III-V's. We hence have a separation

$$E_A(0/-) = \Delta E^{N,N+1}_{MF} + \Delta E^{N,N+1}_{MC} \quad ; \quad E_D(0/+) = \Delta E^{N,N-1}_{MF} + \Delta E^{N,N-1}_{MC} \quad , \qquad (1)$$

where the neutral system A^o has N electrons. Fig. 2c displays the many electron correction $\Delta E^{N,N+1}_{MC}$ for acceptors and the negative of the correction $\Delta E^{N,N-1}_{MC}$ for donors. Finally, $\Delta U_{MC} = \Delta E^{N,N+1}_{MC} - \Delta E^{N-1,N}_{MC}$ is

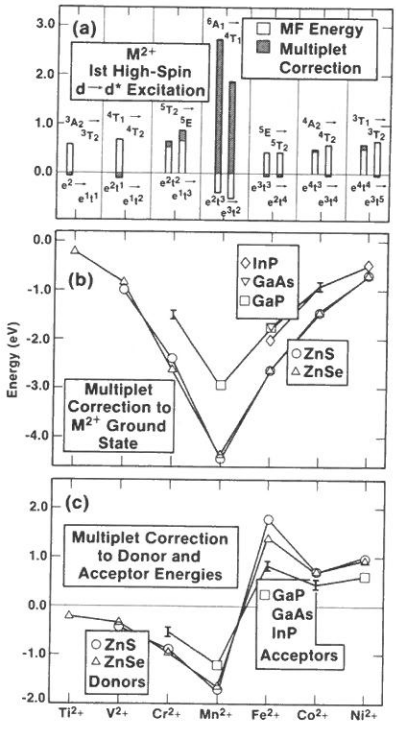

Figure 1 - Comparison of multiplet effects for 3d impurities in II-VI and III-V materials. (a) Energies of the first high-spin transition: II-VI on the left, III-V on right of each column; (b) MC to the ground state of the 2+ oxidation state; (c) MC to transitions between the oxidation states 3+ and 2+ ($A^{+}\rightarrow A^{o}$ in II-VI, $A^{o}\rightarrow A^{-}$ in III-V)

the multiplet correction to the effective Hubbard U for the state with N electrons. Notice that we can use the experimentally observed $E_A(0/-)$ and $E_D(0/+)$ (heavy solid lines in Fig. 2) and the independently calculated multiplet corrections $\Delta E_{MC}^{N,N+1}$ and $\Delta E_{MC}^{N-1,N}$ (Fig. 1c) obtained from from the d→d* spectra, to obtain the mean-field pieces $\Delta E_{MF}^{N,N+1}$ and $\Delta E_{MC}^{N-1,N}$. These are displayed in Fig. 2 as the light solid lines. It is these pieces alone that restricted electronic structure calculations (8-9) should legitimately reproduce.

III. Discussion of Trends

The chemical trends obtained are revealing. **First**, the orbital deformation parameters λ_e and λ_t (1) show that generally $\lambda_e > \lambda_t$ (e orbitals are more localized in tetrahedral symmetry due to absence of σ bonds with nearest neighbors), are approximately equal for a fixed impurity within a class of compounds (e.g. III-V vs II-VI), show an overall decrease with increasing covalency (indicating enhanced hybridization) but a weak dependence on lattice constant (in contrast with the point-ion crystal field theory). The nearly pure d-like λ_e parameter decreases for a given material as the impurity's atomic number increases from Cr to Ni, reflecting the disappearance of the e gap levels into the valence band. The effective crystal field splitting Δ_{eff} increases slowly with covalency. As a function of the impurity, it shows a minimum around the center of the series. These two trends suggest that if substitutional V exists in covalent materials in the 2+ oxidation state, it will show a unique low-spin ground state configuration (^2E), and low-spin excited states for the detectable (high-intensity) transitions. **Second**, the MC to the lowest (high-spin) d→d* excitation energies (shaded areas in Fig. 1a) are generally small except for Mn (as its lowest transition involves a spin flip), are larger for II-VI's than in III-V's, and change sign from one impurity to the other (e.g. the correction reduces the excitation energy for Fe but increases it for Mn). **Third**, MC to the ground state energies (Fig. 1b), while small on the scale of the total energy, are sufficient to stabilize the (Hund's rule) high-spin configurations. This effect is larger in II-VI compounds, hence when a 3d atom dissolves in such

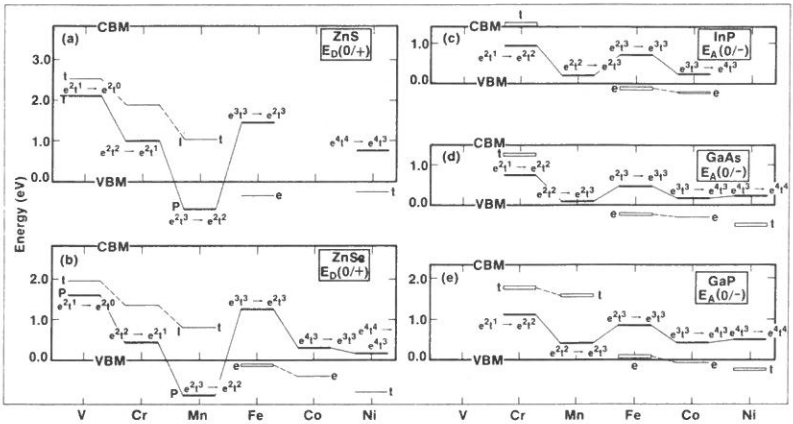

Figure 2 - Observed (heavy solid lines) and MF donor and acceptor energies. T: tentative; I: interpolated; P: predicted.

a crystal, it loses less correlation energy than in a III-V compound, suggesting a larger solubility in the former case. The MC for ground states show a strong dependence on impurity (most negative for the S=5/2 state of Mn), but a negligible dependence on host crystal within a given class. **Fourth,** in contrast to d→d* excitations (Fig. 1a), MC to donor/ acceptor transitions (Fig. 1c) are substantial on the physically relevant energy scale of the band gap, even for covalent materials. [We give in Fig. 1c MC for inverse donor transitions (+/0), N-1→N to emphasize the trends in absolute magnitude]. Clearly, the MC are comparable to MF effects. The change of sign between Fe and Mn reflects the fact that in Mn, energy is gained as a high-spin species is formed in the photoionization process, whereas in Fe, energy is lost as the high-spin state is destroyed. This sign reversal explains the nonmonotonicity in the donor and acceptor energies with atomic number (Fig. 2, heavy solid lines). When subtracting the MC from the observed donor and acceptor energies, we find the level position due to MF effects alone (light lines in Fig. 2). These are purely monotonic, as indeed obtained in mean-field calculations (8-9). The donor level for Mn in II-VI compounds was predicted by interpolating the MF energies from other impurities (1). For Mn in III-V's the figure shows the usually quoted acceptor levels (10).

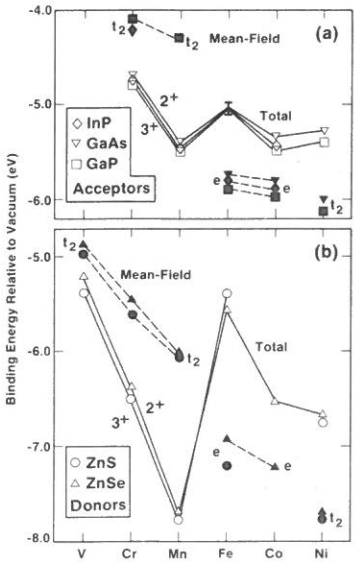

Figure 3 - (a) Acceptor $E_A(0/-)$ and (b) donor $E_D(0/+)$ ionization energies and their mean-field parts, relative to the host vacuum energy.

The clear grouping of many of the characteristics of deep impurities according to host crystal type suggests some universality (10). We show in Fig. 3 the observed 2+/3+ ionization energies in II-VI and III-V compounds, referring them to an approximate vacuum level (using photothreshold data) rather than to the host band edges. We see a striking universality in the trend, where within a class of host crystals the energies for a given impurity are almost constant, the regularities being decided by multiplet effects (c.f. Fig. 1c). Subtracting these effects (i.e., plotting the MF ionization energies $E_{MF}^{N,N+1}$ and $E_{MF}^{N-1,N}$), we see that the reason the II-VI curve is at more negative energies than the III-V curve is predominantly a mean-field effect, as is the larger spread spanned by the transitions in II-VI compounds. Figs. 2 and 3 can be used to predict impurity levels or mean-field levels when they are not known.

IV. The Exchange Correlation Negative Effective U

The substantially negative MC for donor and acceptor energies (Fig. 1c) and consequently to their difference (effective U), particularly for Mn, may have an interesting implication for an effective negative U, as pointed out by us before (1). The mean-field portions of the acceptor transition $E_{MF}^{N,N+1}$ and of the (inverse) donor transition $E_{MF}^{N-1,N}$ in Eq. (1) can have three physical components, represented by the first three terms in Eqs. (2):

$$E_A(0/-) = \left[\Delta E_{ver}^{N,N+1} + \Delta E_R^{N,N+1} + \Delta E_{JT}^{N,N+1}\right] + \Delta E_{MC}^{N,N+1} \qquad (2a)$$

$$E_D(+/0) = \left[\Delta E_{ver}^{N-1,N} + \Delta E_R^{N-1,N} + \Delta E_{JT}^{N-1,N}\right] + \Delta E_{MC}^{N-1,N} . \qquad (2b)$$

The first term represents the change in the vertical (ver) total mean-field energy in the $VB^{p}t^{N} \rightarrow VB^{p-1}t^{N+1}$ acceptor transition and the $VB^{p+1}t^{N-1} \rightarrow VB^{p}t^{N}$ inverse donor transition, respectively, when the lattice is kept unrelaxed. This term does not include any distinct many-electron corrections. Since the wavefunctions are allowed to relax, it does include the changes in the polarization energies, Madelung energies and crystal-field splittings attendant upon the changed screening. The second and third terms ΔE_R and ΔE_{JT} represent changes in the breathing-mode (R) and Jahn-Teller (JT) relaxations, respectively, in the corresponding transitions. The last term represents the many-electron correction. We define the apparent Mott-Hubbard energy $U^{ij}(N)$ for the N-electron system in the usual way, as the energy required to remove an electron from orbital i on the neutral A^o center (transforming it to A^+) and placing it in orbital j of a distant A^o center (transforming it to A^-). In this definition the effective $U^{ij}(N)$ includes Coulomb repulsions, exchange attractions and screening effects. It equals the difference between the acceptor energy $E_A(0/-)$ and the (inverse) donor energy $E_D(+/0)$, both referred to the same origin:

$$U^{(tt)}(N) \equiv E_A(0/-) - E_D(+/0) = \left[U_{ver} + U_R + U_{JT}\right] + \Delta U_{MC} , \qquad (3)$$

where $U_{ver} = E_{ver}^{N+1} + E_{ver}^{N-1} - 2E_{ver}^{N}$; $U_R = \Delta E_R^{N,N+1} - \Delta E_R^{N-1,N}$; $U_{JT} = \Delta E_{JT}^{N,N+1} - \Delta E_{JT}^{N-1,N}$; and $\Delta U_{MC} = \Delta E_{MC}^{N,N+1} - \Delta E_{MC}^{N-1,N}$. The vertical electronic term U_{ver} is positive, reflecting the increased interelectronic repulsion upon adding an electron to the system despite changes in the screening. For most

conventional impurities this is the dominant effect, hence U(N)>0 and the acceptor level is higher in the gap than the donor that belongs to the same center. The "Anderson negative effective U" (11) corresponds to the well known situation in chalcogenide glasses where relaxation effects stabilize the electron-rich configuration more than the electron-poor configuration (i.e. the positive U_{ver} is outweighed by the negative $U_R + U_{JT}$), leading to the metastability of the latter. In nonequilibrium situations (i.e. optical excitations) where no static lattice relaxation occurs, this mechanism does not apply. We wish to point out the possibility of a different type of negative effective U where many-electron effects, present also in nonequilibrium situations, outweigh (with possible help from $U_{JT} + U_R$) the electronic U_{ver}, leading to an overall U<0. Transition atom impurities in semiconductors are special in this sense in three ways. First, a self regulating response (9) of the valence band resonances reduces the MF value U_{ver} dramatically [U_{ver} ~0.5-1.0 eV (9)] relative to the values in ionic media or free ions ($U \sim 10$ -22eV). Second, JT energies appear to be small [e.g., in the best studied case of Cr d^4 ($^5T_2$) in II-VI materials it is ~0.06 eV (12a); for the $^5T_2 \rightarrow {}^6A_1$ transition, $\Delta E_{JT} + E_R \tilde{=}$ - 0.3 to -0.4 eV (12b)]. Third, because of their localization, multiplet effects (including exchange splitting) are large (~ -1 eV, c.f. Fig. 2c). This suggests that even if lattice rearrangements alone are insufficient to produce a negative (Anderson) effective U, many-electron effects can produce an "exchange correlation negative effective U" if $U_{ver} < [U_R + U_{JT} + \Delta U_{MC}]$.

We see from Fig. 1b that Mn is the most likely impurity to show such an effect. For substitutional Mn in III-V's we have three charge states: the neutral impurity [A^o,d^4,e^2t^2,$^5T_2$] appearing as the 3+ oxidation state, the singly positive impurity [A^+,d^3,e^2t^1,$^4T_1$] appearing as the 4+ oxidation state, and the singly negative impurity [A^-,d^5,e^2t^3,$^6A_1$] appearing as the 2+ oxidation state. The dominant ground state orbital configurations e^nt^m and the multiplet assignments were determined from the preceding analysis of the absorption data. We denote A^+, A^o and A^- as N-1, N, and N+1, respectively (for Mn, N=4). We calculate from the spectra $\Delta E_{MC}^{4,5} = -1.25$ eV and $\Delta E_{MC}^{3,4} = 0.6$ eV, or $\Delta U_{MC} = -0.65$ eV. Using the estimate quoted above $\Delta E_R^{N,N+1} + \Delta E_{JT}^{N,N+1} \tilde{=} -(0.3\text{-}0.4)$eV from II-VI materials and neglecting $\Delta E_R^{N-1,N} + \Delta E_{JT}^{N-1,N}$ (the $^4T_1 \rightarrow {}^5T_2$ transition is expected to have a smaller net relaxation difference), we find that if $U_{ver} \lesssim 1$ eV the system will have an overall negative effective U, whereas without MC, we have U>0. Recent MF calculations for GaP (9a) predict U_{ver} values in this range. If U<0, it means that the Mn^{3+} [A^o, $^5T_2$] state is never the ground state, for any value of the Fermi energy E_F.

We can distinguish two situations for U<0. First, if $E_A(0/-)>0$ ("type I negative U") A^o is stabler than A^- if the system is isolated, however, $E_D(+/0)>E_A(0/-)>0$, so in contact with the Fermi sea the total energy of A^o is never the ground state (although nonequilibrium experiments can detect it). In this case, [A^+, $^4T_2$] is the ground state for low E_F, and after the transition point, [A^-, $^6A_1$] is the ground state. In the second case ("type II negative U") A^o is unstable relative to A^- already in the isolated system, with $E_A(0/-)<0$ (i.e. acceptor in the valence band), hence A^o will not be detected even in nonequilibrium experiments [In this case it is possible that the A^+ center is never in the gap for any E_F, and only A^-, $^6A_1$ is observed for all E_F]. This will happen if the gain in energy from lattice rearrangements and MC outweigh the electron repulsion in the $E_A(0/-)$ transition in Eq. (2a). Using the same numbers as above, this means

that $\Delta E_{ver}^{4,5} \lesssim 1.6$ eV. Recent MF calculations (9a) show that this is close to, but probably not the case for GaP:Mn, but could be the case for GaAs:Mn. Notice that in "type II negative U" the conventional $E_A(0/-)$ (i.e. $^5T_2 \rightarrow {}^6A_1$ for Mn) is in the valence band. In other words, the remaking of bonds cannot provide enough energy to transform the atom entering the crystal (d^5s^2 if Mn) into the neutral state (d^4) and lower energies are attained by the configuration [A^-+hole]. The observed (positive) acceptor, as suggested by Kaufmann and Schneider (13), could correspond to this ground state of the type ($^6A_1$ + hole) transforming into $^6A_1$. Notice further that a type II negative U is consistent with the fact that the A^- state is always observed by EPR (14) in nominally p-type samples for GaAs, InP and GaP. In GaAs:Mn another spectrum is also observed, corresponding to $g \tilde{=} 5.85$ (14b). We point out that this spectrum, interpreted (14b) as the $^4T_1$ ground state of interstitial Mn (d^7) could be interpreted equally well as the $^4T_1$ ground state of substitutional Mn (d^3) the A^+ center. Note that if the system is a type II negative U, the observation of the d^5 configuration of Mn does not mean that the sample is n-type, as usually assumed.

Acknowledgments: This work was supported by DOE Contract No. DE-AC02-83CH10093. A. Fazzio and M. J. Caldas acknowledge support from Fundação de Amparoá Pesquisa do Est. S. Paulo (FAPESP).

+Permanent Address: Instituto de Física (Depto Fís. Estado Sólido), UNICAMP, Campinas, SP, Brasil; §Permanent Address: Instituto de Física (Depto Fís. Materiais e Mecânica), USP, Cid. Universitária, São Paulo, SP, Brasil.

References

(1) (a) A. Fazzio, M. J. Caldas and A. Zunger, Phys. Rev. B 29, 5999 (1984) (b) ibid, in press.
(2) S. Sugano, Y. Tanabe and H. Kamimura, "Multiplets of Transition-Metal Ions in crystals" (Academic Press, New York) 1970.
(3) L. A. Hemstreet and J. P. Dimmock, Phys. Rev. B 20, 1527 (1979).
(4) A. G. O'Neill and J. W. Allen, Solid State Commun. 46, 833 (1983).
(5) J. C. Slater, "The Self-Consistent Field for Molecules and Solids", vol. 4 (McGraw-Hill, New York) 1974, p. 39.
(6) J. S. Griffith, "The Theory of Transition Metal Ions", (Cambridge University Press, Cambridge) 1971.
(7) U. von Barth, Phys. Rev. A 20, 1693 (1979).
(8) A. Fazzio and J. R. Leite, Phys. Rev. B 21, 4710 (1980); A. Zunger and U. Lindefelt, Phys. Rev. B 27, 1191 (1983).
(9) (a) A. Singh and A. Zunger (to be published); (b) A. Zunger and U. Lindefelt, Solid State Comm. 45, 343 (1983).
(10) L. A. Ledebo and B. K. Ridley, J. Phys. C 15, L961 (1982); M. J. Caldas, A. Fazzio and A. Zunger, Appl. Phys. Lett. (In Press).
(11) P. W. Anderson, Phys. Rev. Lett. 34, 953 (1975).
(12) (a) M. Kamińska, J. M. Baranowski, S. M. Uba and J. T. Vallin, J. Phys. C 12, 2197 (1979); (b) M. Godlewski and M. Kamińska, J. Phys. C 13, 6537 (1980).
(13) U. Kaufmann and J. Schneider, Adv. Electronics and Electron Physics, 58, 81 (1981).
(14) (a) V. F. Masterov, S. B. Mikhrin, B. E. Samorukov and K. F. Shtelmakh, Sov. Phys. Semicond. (1983); (b) V. F. Masterov, Yu. V. Maltsev and V. K. Sobolevskeii, Sov. Phys. Semicond. 15, 1235 (1981).