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Empirical laws and their theoretical justification for the crystal-field splitting and ionization energy of transition-metal ions in semiconductors

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It is pointed out that the ionization energy and crystal-field splitting of substitutional transition-metal impurities (TM) in semiconductors are simply related to the interatomic distance and ionicity of the perfect crystal. A theoretical justification of these empirical laws is provided through the use of both a simple molecular model and a full tight-binding Green's-functions calculation. The results confirm the validity of Harrison's $d^{-7/2}$ semiempirical law for the interaction between the TM atom and its neighbors. Linear plots can then be drawn for each TM impurity giving a simple and useful method for predicting these spectroscopic quantities in unknown cases.

Two central spectroscopic quantities that characterize transition-metal (TM) impurities in semiconductors are the crystal-field splitting Δ and the ionization energy E_I. Although numerous experimental data already exist[1-3] there have been only few attempts to rationalize them.[4-6] A first aim of this work is to show that there exist some rather accurate experimental laws allowing the determination of these quantities. The first one is that the product of $E_I\Delta$ for one TM in different semiconductors is proportional to d^{-7} where d is the nearest-neighbor's distance. This is in direct connection with Harrison's semiempirical rule[7] for tight-binding interatomic interactions. The second law corresponds to the fact that the crystal-field splitting Δ is a quasilinear function of the bulk-crystal ionicity.

Although there have already been several attempts to understand the electronic structure of these impurities[8-11] these have been mainly numerical computations predicting trends for a transition series in one given semiconductor. Furthermore, such attempts are not well suited to the derivation of simple analytical laws such as those which will be obtained here. Recently, however, a renormalized molecule model of these impurities has been shown to give a fairly accurate physical picture of these impurities[12] and was subsequently used to provide a link between TM levels and heterojunction valence-band offsets.[13] Here we shall provide a justification of the theoretical laws based on a tight-binding approach with two levels of sophistications: (i) a simple molecular description directly showing the origin of the analytical law, (ii) a full Green's-function calculation proving the validity of the simple model.

The first empirical law concerns the product $E_I\Delta$ which turns out to be proportional to d^{-7}, at least for a given impurity in different semiconductors. This is verified on Fig. 1 where the product $E_I\Delta$ for Cr^{2+} ($^5T_2 \rightarrow {}^5E$) and Co^{2+} ($^4A_2 \rightarrow {}^4T_2$) is plotted versus d^{-7}. This is then confirmed by Fig. 2 for Ni (d^8) in several semiconductors where a slope equal to -7 is again found. To check that that theory is able to reproduce such trends we have first performed a full tight-binding Green's-functions calculation as described in Ref. 14. The calculated points on Fig. 1 are in good agreement with experiment. However, as for local density (LD) calculations, this does not explain simply the physical origin of the analytical laws. This can however be done if we take the tight-binding view that the

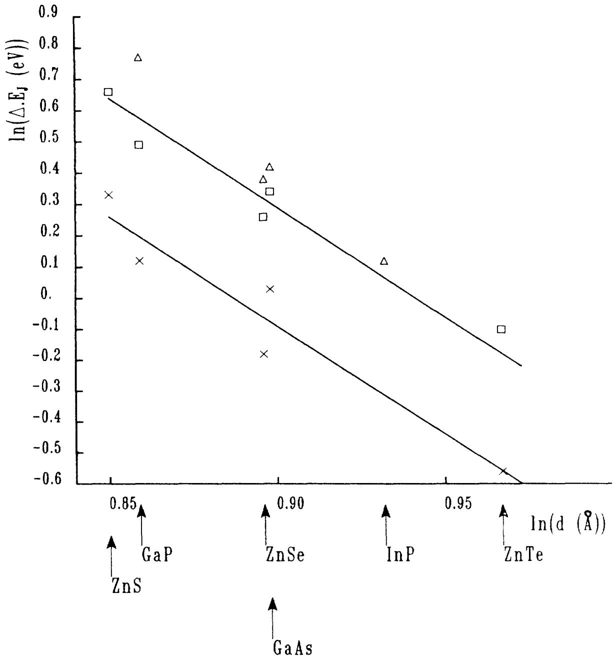

FIG. 1. Plot of $\ln[E_J\Delta\ (\mathrm{eV}^2)]$ vs $\ln[d\ (\text{Å})]$ (interatomic distance) where Δ is the energy of the zerophonon line of the transitions $^5T_2 \rightarrow {}^5E$ for Cr^{2+} (□, experimental; △, calculated) and $^4A_2 \rightarrow {}^4T_2$ for Co^{2+} (×) in various semiconductors.

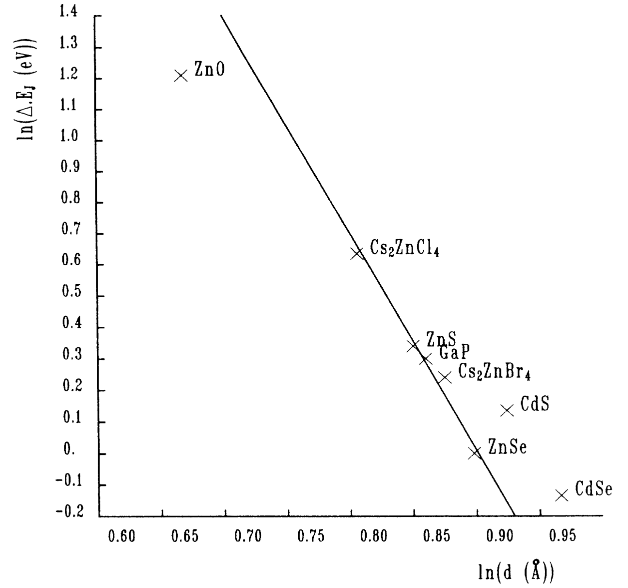

FIG. 2. Same as Fig. 1 for Ni^{2+} ($^3T_1 \rightarrow {}^3T_2$).

transition-metal level structure is due to the interaction between the atomic states of energy E_d and the crystal states. As described in Ref. 12 the TM states of E symmetry remain practically uncoupled at the energy E_d. On the other hand, the T_2 atomic d states are coupled and one can describe this coupling by writing the wave function ψ as

$$\psi = a_d\phi_d + \sum_\alpha a_\alpha \phi_\alpha \ , \tag{1}$$

where ϕ_d is the d atomic state and the ϕ_α belong to the remaining crystal. Eigenstates can be obtained from the set of equations

$$\begin{aligned} (E - E_d)a_d &= \sum_\alpha V_{d\alpha} a_\alpha \ , \\ (E - E_\alpha)a_\alpha &= V_{\alpha d} a_d \ . \end{aligned} \tag{2}$$

Eliminating a_α one gets

$$E = E_d + \sum_\alpha \frac{|V_{d\alpha}|^2}{E - E_\alpha} \ . \tag{3}$$

To derive the empirical law we use the fact that the neighbors of the TM impurity are the anions and that T_2-like combinations of the anion states mainly belong to the top of the valence band. One makes little error then by replacing E_α in (3) by the top of the valence band E_v which leads to

$$(E - E_d)(E - E_v) = \sum_\alpha |V_{d\alpha}|^2 \ . \tag{4}$$

This equation has two roots, the filled t_2 bondinglike level of energy E_{t_2} and the antibondinglike $E_{t_2^*}$. The crystal-field splitting is, thus, given by

$$\Delta = E_{t_2^*} - E_d \ , \tag{5}$$

while the ionization energy from the valence band is

$$E_I = E_{t_2^*} - E_v \ . \tag{6}$$

From (4) we, thus, obtain directly

$$E_I \Delta = \sum_\alpha |V_{d\alpha}|^2 \ . \tag{7}$$

If we make use of a nearest-neighbor's tight-binding model and apply Harrison's empirical law (Ref. 7), $\sum_\alpha |V_{d\alpha}|^2$ will scale like d^{-7} in perfect agreement with the empirical law. Of course our derivation is oversimplified and for this reason we have performed a complete tight-binding Green's-function calculation which, for TM impurities in Si gives results comparable to those of LD calculations.[11] We have used a spin unrestricted scheme[14] and calculated Δ and E_I with Slater's transition state procedure. The calculated values are given on Fig. 1 and confirm the validity of the simplified approach.

The second empirical law we have found is between the crystal-field splitting Δ and Phillip's ionicity F.[15] Figure 3 clearly shows for Cr^{2+} and Co^{2+} that the correlation is practically linear. As shown on the same figure the results of Green's-functions calculations give the same linear dependence $\Delta(F)$ except for a constant shift which can be explained by the multiplet correction (this one should be constant for the Cr^{2+} internal transition since the localization of the gap states remains practically constant). Although such an agreement is already valuable in itself we can still gain more physical insight through the use of a simplified model. This one is based on the well-known molecular or bond orbital model of tetrahedral semiconductors where sp^3 orbitals are coupled in pairs as in diatomic molecules.[16] In such cases the electron population

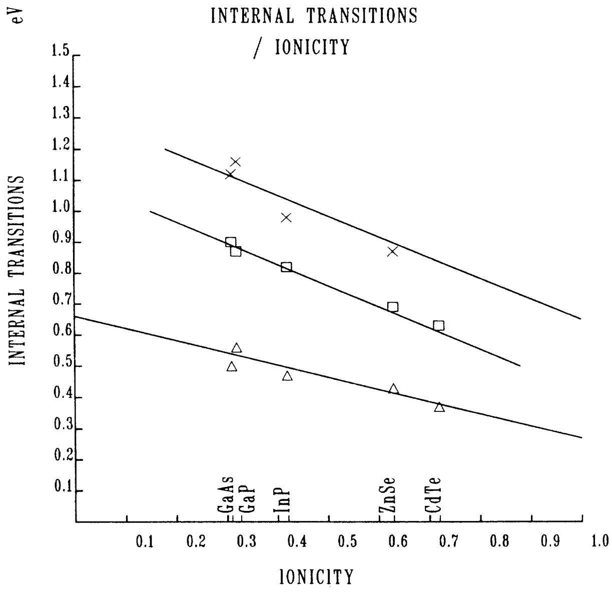

FIG. 3. Relationship between the effective crystal-field splitting and the ionicity for Cr^{2+} ($^5T_2 \rightarrow {}^5E$) (□, experimental; ×, calculated) and for Co^{2+} ($^4A_2 \rightarrow {}^4T_2$) (△, observed).

on the anion is given, for the perfect crystal, by

$$N_A = 4(1+\sqrt{F}) \ , \tag{8}$$

where F is the ionicity defined as

$$F = \frac{(\Delta E)^2}{(\Delta E)^2 + 4\beta^2} \ , \tag{9}$$

where ΔE is the difference in sp^3 energies of the anion and cation and 2β is the bonding-antibonding gap. If we treat the defect in the same molecular model, the t_2 d states of the TM impurity will interact with the sp^3 orbitals of the anion. For each component of the t_2 states one gets a 2×2 matrix

$$\begin{bmatrix} E_d & V \\ V & E_A \end{bmatrix} \ , \tag{10}$$

where V is the strength of the "d"-sp^3 coupling and E_A is the sp^3 energy of the anions. The eigenstates of this matrix are the molecular model approximations to E_{t_2} (bonding state) and $E_{t_2^*}$ (antibonding state) discussed above. Calling $\delta = (E_A - E_d)/2$ and using (10) we get for the crystal-field splitting

$$\Delta = \delta + \sqrt{\delta^2 + V^2} \ . \tag{11}$$

In principle E_d has to be obtained in a self-consistent way. However, as was noted earlier[12] screening in such materials is efficient enough so that the final situation is such that each atom is practically neutral. The simplest approximation is, thus, to fix E_d by a condition of charge neutrality on the TM atom, or equivalently to impose that the number of electrons on the four anions sp^3 orbitals is equal to N_A, the bulk value. This means that each component of the T_2 states must bring $N_A/4$ on the anion sp^3 orbitals since, on the same grounds, there is already $N_A/4$ brought by the A_1 states which are not explicitly considered in the model (this is discussed in detail in Ref. 12). The neutrality condition becomes

$$\frac{N_A}{4} = \frac{n_{t_2}}{6} \left[\frac{\delta}{(\delta^2+V^2)^{1/2}} \right] + \frac{n_{t_2^*}}{6} \left[1 + \frac{\delta}{(\delta^2+V^2)^{1/2}} \right] \ , \tag{12}$$

where $n_{t_2} = 6$ is the electron occupation of the bonding t_2 state and $n_{t_2^*}$ of the t_2^* antibonding state. Solving (12) for δ and injecting the result into (11) gives the extremely simple law

$$\Delta = V[(1-K)/(1+K)]^{1/2} \ , \tag{13}$$

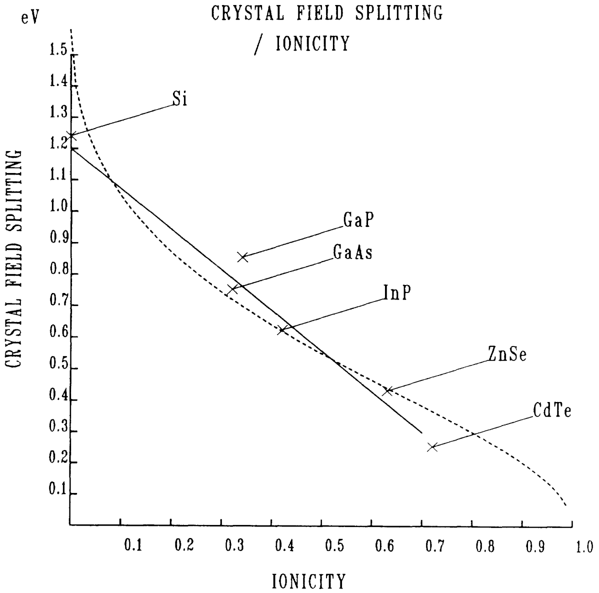

FIG. 4. Crystal-field splitting vs the ionicity for Cr^{2+} ($^5T_2 \rightarrow {}^5E$). Results are taken from molecular model (dashed line) and from self-consistent Green's-functions calculation (crosses).

with K defined by

$$K = |(6\sqrt{F} - n_{t_2^*})/(6 - n_{t_2^*})| \ . \tag{14}$$

Obviously the approximation is mainly valid for relatively small $n_{t_2^*}$ where the bond can polarize effectively. Figure 4 shows that the results for Cr^{2+} are fairly close to those of the spin-restricted Green's-functions calculation and that Δ is quasilinear with F. Furthermore, expression (13) does not take into account the spin polarization which greatly influences the slope of the straight line (see Fig. 3). Nevertheless, it is clear that screening effects (corresponding to the neutrality condition) are very important and are responsible for the linear behavior with F.

In conclusion, we have shown that the crystal-field splitting and ionization energy of transition-metal impurities in semiconductors can be simply related to bulk quantities like the interatomic distance and ionicity. We have obtained two empirical laws and have shown that these can be justified theoretically. Thus, we believe that these laws can be used to predict the position of the levels in materials where they have not yet been observed.

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