

Calculation of Impurity States in ZnO Using Recursive Green's Function

Chih-Iai Yang¹, Kian S. Dy², and S. Y. Wu³

¹*Physics Group, Department of General Studies,
Chang Gung College of Medicine and Technology,
Kueishan, Taoyuan, Taiwan 333, R.O.C.*

²*Department of Physics & Astronomy, University of North Carolina,
Chapel Hill, NC 27599-3255, U.S.A.*

³*Department of Physics, University of Louisville,
Louisville, KY 40292, U.S.A.*

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The impurity states of a single Cr and Mn atom in a simulated ZnO crystal are calculated by using the real space recursive Green's function and Linear Muffin-Tin Orbitals method. The results show that most of the impurity states are in the ZnO band gap and could significantly affect the conduction of a ZnO-based varistor.

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The nonlinear electrical conduction of ZnO-based varistor has long been investigated by experimentalists [1-6]. It is well known that impurities in ZnO are closely related to the nonlinearity [1-3], which exhibits high resistance at low voltage and low resistance at high voltage. The electronic structures of impurities in ZnO are therefore essential for better understanding of the conduction mechanism. There have been several articles [7-11] devoted to the investigation of transition metal (TM) impurities in ZnO. Most of them used the cluster method and zinc-blende structure. Recently, Bertinello et al. [11] used the LCAO molecular-cluster approach to calculate the electronic structure of a substitutional Cu impurity in hexagonal ZnO and obtained very accurate results. In this article, we also maintain the actual hexagonal wurtzite structure of ZnO and simulate the bulk nature of ZnO crystal in the calculation. The goal is to use the recursive Green's function to calculate the local density of states of a substitutional TM impurity atom in ZnO crystal.

We first give a brief review of how the recursive Green's function method, as developed by Dy, Wu and Spratlin [12,13], is applied to the calculation. For a system with Hamiltonian H , the Green's function is defined as the following:

$$G(z) = (z - H)^{-1}, \quad (1)$$

where z is a complex number. The density of states $D(E)$ can be derived from the Green's function by

$$D(E) = -\frac{1}{\pi} \lim_{\epsilon \rightarrow 0} \text{Tr} \text{Im} G(E + i\epsilon), \quad (2)$$

where Tr and Im denote the trace and imaginary part, respectively.

Consider first a small system with Hamiltonian $H^{(n)}$ and Green's function $G^{(n)}$ which can be easily calculated using standard procedures. We next change the system by adding to it a layer of atoms. The Hamiltonian for the larger system now becomes:

$$H^{(n+1)} = \begin{pmatrix} H^{(n)} & V \\ V^+ & h \end{pmatrix}, \quad (3)$$

where h is the Hamiltonian of the added layer and V is the coupling of the layer to the subsystem. Then, using the recursive equations, the Green's function $G^{(n+1)}$ of the enlarged system can be calculated by

$$G^{(n+1)} = \begin{pmatrix} G_{11}^{(n+1)} & G_{12}^{(n+1)} \\ G_{21}^{(n+1)} & G_{22}^{(n+1)} \end{pmatrix}, \quad (4)$$

where,

$$G_{22}^{(n+1)} = [(z - h) - V^+ G^{(n)} V]^{-1}, \quad (5)$$

$$G_{12}^{(n+1)} = G^{(n)} V G_{22}^{(n+1)}, \quad (6)$$

$$G_{21}^{(n+1)} = G_{22}^{(n+1)} V^+ G^{(n)}, \quad (7)$$

$$G_{11}^{(n+1)} = G^{(n)} + G_{12}^{(n+1)} V^+ G^{(n)}. \quad (8)$$

Thus, using this recursive set of equations, we can perform our calculation using small matrices while enlarging the system until it includes the whole system or until it converges for the case of infinite system.

For practical reasons, we perform calculation for a system of limited size, which, however, simulates the infiniteness of the crystal structure. This can be achieved by constructing a supercell based on the ZnO wurtzite lattice and applying periodic boundary conditions that make it look like a ZnO crystal. Our supercell contains 120 atomic spheres, 40 each of Zn, O, and empty spheres. The introduction of empty spheres into the supercell is an integral part of the calculation [14], which remedies the muffin-tin approximation in an open structure like the wurtzite. In Fig. 1, one of the 5 layers in the supercell is illustrated,

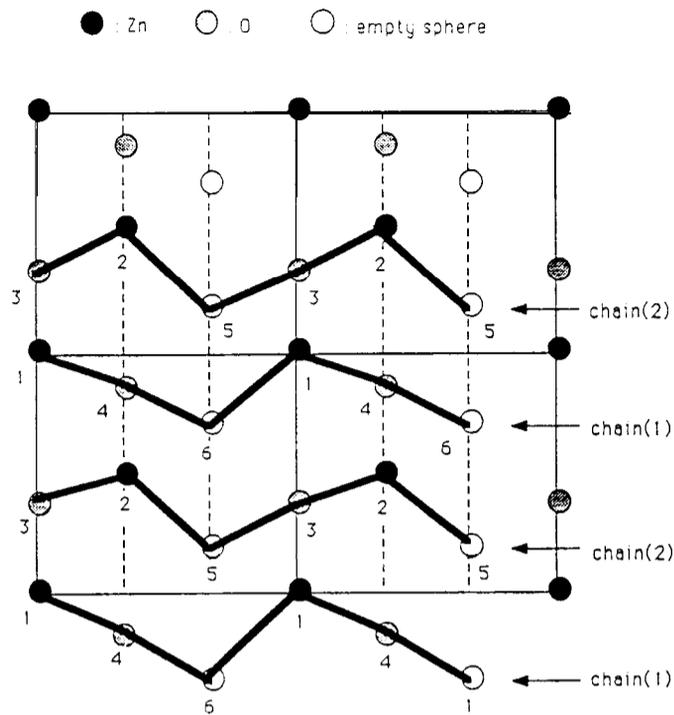


FIG. 1. Schematic depiction of a layer in the supercell.

where two types of chains, labeled (1) and (2), are specified. There are in total 4 chains in a layer and each chain contains 6 atomic spheres.

Two transition metal atoms, Cr and Mn, are calculated respectively, each going into the supercell substitutionally for Zn. The Hamiltonian is formulated using real space linear muffin-tin orbitals with self-consistent potential parameters [15]. The real space method not only greatly simplify the formulation but, coupled with recursive Green's function also, considerably enhance the computing efficiency [13].

In Fig. 2, the local density of states of Cr in ZnO is presented, where the splitting of E and T_2 states is immediately identified. The separation of the states is approximately 0.68 eV, which is generally consistent with the literature data [7-11] of TM impurity states in ZnO. Consider, for example, the separation reported by Gemma[7], which is about 0.72 eV. The two states are mostly populated by $3d$ electrons, as shown in Table I, with a very small amount of p electrons and an almost negligible contribution coming from the s orbital. The position of the E state, measured with respect to the top of valence bands of ZnO, is about 2.45 eV. This is done by comparing the bands derived from intrinsic ZnO with that

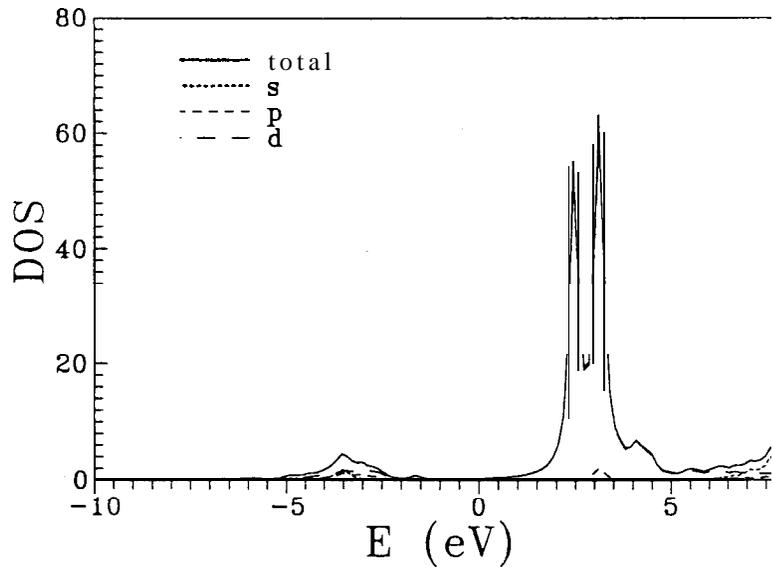


FIG. 2. Density of states of a single impurity Cr in ZnO crystal.

TABLE I. The E and T_2 states of Cr and Mn in ZnO and the contributions from the s , p , and d orbitals.

		Cr				Mn	
		eV	γ_0	eV		γ_0	
T_2	3.13	s	0.2	T_2	2.18	s	0.2
		p	3.2			p	3.0
		d	96.6			d	96.8
E	2.45	s	0.2	E	1.50	s	0.1
		p	0.5			p	0.4
		d	99.3			d	99.5

from impurity Cr. Here we also define the zero of energy as the top of ZnO valence bands. Since the band gap of ZnO is around 3.40 eV, it is obvious that both E and T_2 states of Cr are within the gap region. We calculate the number of states of Cr up to the energy of the bottom of ZnO conduction bands. And it is found that approximately 3.70 electrons are

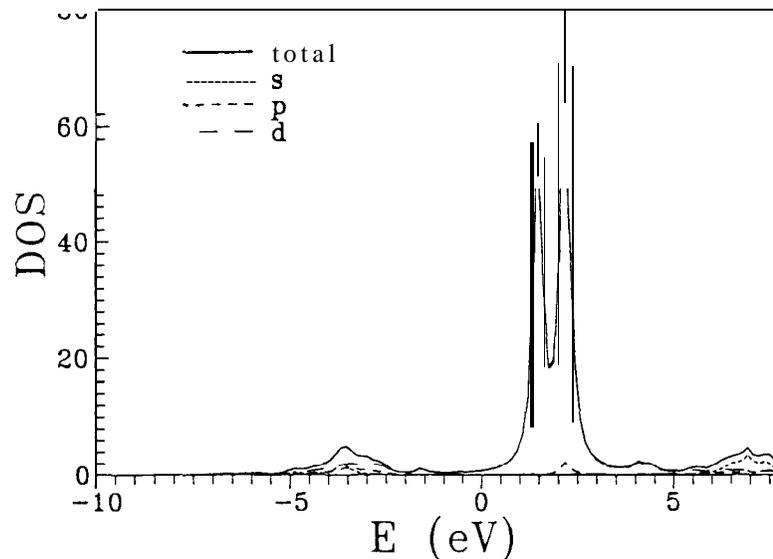


FIG. 3. Density of states of a single impurity Mn in ZnO crystal.

needed to fill up these states. This suggests that the impurity is likely to become the ion $\text{Cr}^{3+}(d^3)$, losing two d electrons and one s electron, when the Fermi level is located in the upper part of the gap region.

In the case of Mn impurity, the splitting is the same value of 0.68 eV and 3 d electrons also occupy almost exclusively the states, as can be checked out from Fig. 3 and Table I. However, the E state is 1.50 eV above the top of ZnO valence bands and is 0.95 eV lower than the E state of Cr. This result is also consistent with literature data pertaining to TM impurities in III-V semiconductors. In particular, the splitting reported by Gemma [7] is 0.75 eV. However, his values, including that of Cr mentioned in the previous paragraph, are derived from a less accurate procedure, as explained by Bertonecello et al. [11]. The number of electrons occupying the states below the bottom of ZnO conduction bands is around 4.50, which means that the Mn impurity atom is most likely the ion $\text{Mn}^{3+}(d^4)$ losing two d electrons and one s electron for a Fermi level in the gap region.

In summary, we have successfully developed a real space method to calculate the impurity states of Cr and Mn in ZnO by combining the recursive Green's function with LMTO. The wurtzite structure and the bulk nature are incorporated into our calculation. The results show that the impurity states E and T_2 of Cr and Mn are located in the gap region of ZnO and that Mn and Cr are ions for a Fermi level in that region. In a ZnO-based varistor, some electrons released from the impurity ions could move to occupy the

surface or interface states at the ZnO-ZnO grain boundaries, which, according to Cordaro et al. [2] may be in a Gaussian distribution centered approximately at 1.3 eV below the conduction bands. The electrons trapped on these states thus form the schottky barriers which partly give rise to the nonlinear conduction. We will continue to improve the self-consistent procedures and to try different impurity atoms in future calculations.

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