

Spin-polarized electronic structure of Cr impurities in ZnS

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A unified picture of the electronic structure of Cr impurities in ZnS is presented on the basis of first-principles spin-polarized Green's-function calculations. The results obtained on physical properties (donor and acceptor ionization energies, hyperfine coupling constants, g values, and Jahn-Teller distortion) are in good agreement with the experimental data, and further clarify the interplay between ionicity and covalency in II-VI compound semiconductors.

II-VI compound semiconductors possess potential importance in application to opto-electronic devices because of the wide variety of their fundamental energy gaps (2–4 eV).^{1,2} Deep levels induced by transition-atom (TA) impurities are promising candidates to realize, e.g., a blue light-emitting diode. These materials, on the other hand, are rather unusual in their physical properties, since both covalency and ionicity play an important role. The TA impurity is thus a microscopic probe to clarify characteristic features of the host II-VI semiconductors. The amount of hybridization between d orbitals of the TA impurity and extended wave functions of the host semiconductor is an essential quantity to determine the electronic and magnetic properties of this system: ionization energy, hyperfine coupling constants, and g values that may be anisotropic due to Jahn-Teller (JT) lattice distortion. In spite of these interesting features of these materials, understanding of the electronic structure of a TA impurity in II-VI compound semiconductors is not yet satisfactory. This is partly ascribed to the difficulty in preparing p - and n -type samples with good quality: lattice defects are likely to be induced by impurity doping, probably due to the ionic character of the host materials. From a theoretical point of view, the lack of reliable electronic-structure calculations impedes proper interpretation of the observed optical spectra: electronic-structure calculations for a TA impurity in II-VI compound semiconductors performed so far are limited to the empirical tight-binding scheme³ or the cluster approximation,⁴ neither of which can describe quantitatively the electronic structure of the TA impurity in an otherwise perfect crystal. Thus, reliable first-principles calculations are required to interpret and predict variety of physical phenomena inherent in a TA impurity in II-VI compounds.

We here report a first-principles Green's-function calculation⁵ on the spin-polarized electronic structure of the substitutional and Jahn-Teller-distorted Cr impurity in ZnS. A Green's matrix scheme⁶ has been implemented, and the previous results⁷ obtained by this method for the defects in Si are reproduced. The present calculation

is performed within the local spin-density functional formalism⁸ with norm-conserving pseudopotentials.⁹ The basis set employed here consists of Gaussian orbitals situated at atomic sites. We use s , p , and d Gaussian orbitals for Zn and S atoms: three exponents for each l in the case of Zn, and two exponents for s and p orbitals and one exponent for d orbital in the case of S.¹⁰ This basis set satisfactorily reproduces the overall band structure of the host ZnS (Table I). In the impurity Green's-function calculation, the Gaussian orbitals which are placed at the Zn site in the host calculation are adopted for a Cr impurity. The basis orbitals located at the impurity site and the first-neighbor sites are retained to express Green's operator.¹² In the case that the Jahn-Teller effect is relevant, the amount of distortion is determined by combining¹³ the first-principles Green's-function calculation on the electronic structure with the semiempirical Keating model¹⁴ to evaluate the force constants.

Figure 1 shows the occupancy level structure of the Cr impurity at the Zn substitutional site in ZnS. It is found that three types of charge states are stable for the Cr impurity: Cr^+ (the formal charge of this state is -1 ; i.e., A^-),¹⁵ Cr^{2+} (A^0), and Cr^{3+} (A^+) depending on the location of the Fermi level in the energy gap. The donor ionization level $\epsilon(0/+)$ and the acceptor ionization level $\epsilon(-/0)$ lie 1.0 and 2.2 eV, respectively, above the top of the valence bands ϵ_v . The calculated values

TABLE I. Calculated eigenvalues in eV relative to the top of the valence bands for ZnS compared with experiments (Ref. 11). The width of the calculated d bands is about 2 eV.

	Γ_1	Γ_{15}	Γ_1	X_1	X_5
Theory	-12.1	0.0	3.4	-10.6	-2.4
Expt.	-13.5	0.0	3.7	-12.0	-2.5
	X_1	L_1	L_3	L_1	Zn(3d)
Theor.	4.0	-11.0	-1.0	3.9	-6.0
Expt.	4.1	-12.4	-1.4	4.0	-9.0

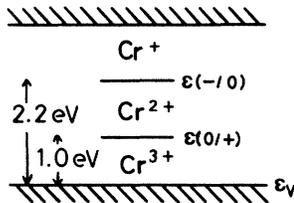


FIG 1. Calculated occupancy levels of a Cr impurity in ZnS. Experimental values for $\epsilon(-/0)$ diverge in the range from 2.4 to 3.0 eV (Refs. 16–18).

are consistent with the experimental values, although the observed data disagree with each other considerably.^{16–18} The effective Hubbard U in the present calculation [$U = \epsilon(-/0) - \epsilon(0/+)$] is 1.2 eV, approximately four times greater than that of 3d TA impurities in Si (i.e., 0.3 eV).¹⁹ This difference is caused by the localized nature of the gap state in ZnS compared with the case in Si, whereas the Hubbard U in ZnS is much smaller than that in free TA ions²⁰ because of hybridization with the host orbitals.

Figure 2 shows the single-electron energy-level structure of $\text{Cr}^{3+}(d^3)$, $\text{Cr}^{2+}(d^4)$, and $\text{Cr}^+(d^5)$ impurities in ZnS. In the case of the ideal (undistorted) Cr impurity, the doublet e and triplet t_2 exist in the energy gap. It is found that the high-spin state is stable against the low-spin state for all the possible charge states of the Cr impurity. (The total energy evaluated within the present Green's-function scheme for the high-spin state is about 3 eV lower than that for the low-spin state in the case of the ideal Cr^{2+} .) The exchange splitting energy [$\Delta_X \equiv \epsilon(e_-) - \epsilon(e_+) = 3.2$ eV] exceeds the crystal-field splitting energy [$\Delta_{CF} \equiv \epsilon(t_{2+}) - \epsilon(e_+) = 0.7$ eV]. This

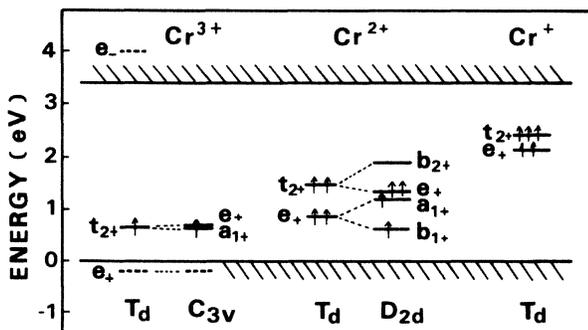


FIG. 2. Level structure in the energy gap of ideal and Jahn-Teller-distorted Cr impurities in ZnS.

indicates that the localization due to ionicity overcomes the delocalization due to covalency. The calculated crystal-field splitting energy Δ_{CF} corresponds to the excitation energy of the intra-atomic $d \rightarrow d^*$ transition, from 5T_2 to 5E in the case of Cr^{2+} , which is 0.64 eV from optical measurement.²¹

Jahn-Teller lattice distortion²² can occur in the cases of $\text{Cr}^{3+}(d^3, {}^4T_1)$ and $\text{Cr}^{2+}(d^4, {}^5T_2)$ where the triplet t_{2+} is partially occupied by one and two electrons, respectively. Since electron-paramagnetic-resonance (EPR) measurements on TA impurities in II-VI compound semiconductors suggest tetragonal (D_{2d}) JT distortion for the d^4 charge state^{23,24} and trigonal (C_{3v}) distortion for the d^3 charge state,²⁵ we here consider tetragonal and trigonal distortions for Cr^{2+} and Cr^{3+} , respectively.²⁶ The theoretically determined distortions are $Q_{tet} = -0.16 \text{ \AA}$ for Cr^{2+} and $Q_{tri} = 0.05 \text{ \AA}$ (Ref. 27) for Cr^{3+} , and the resulting gains in total energy become 1500 cm^{-1} for Cr^{2+} and 65 cm^{-1} for Cr^{3+} . The theoretical value is in reasonable agreement with the experimental data for Cr^{2+} ,^{23,24} while no available data exist for Cr^{3+} . Due to tetragonal distortion, the doublet e_+ splits into two singlets a_{1+} and b_{1+} , and the triplet t_{2+} splits into a singlet b_{2+} and a doublet e_+ in the case of Cr^{2+} (Fig. 2). Since two electrons should be accommodated in either the b_{2+} or e_+ state, the level ordering shown in Fig. 2 [i.e., $\epsilon(b_{2+}) > \epsilon(e_+)$] is energetically favorable. This level-ordering combines with depairing distortion of the surrounding S atoms. In the case of Cr^{3+} , the trigonal JT distortion is quite small: the slight inward distortion of the triangle of the neighboring S atoms in the (111) plane, along with stretching of the Cr—S bond length along the [111] direction, results in $\epsilon(e_+) > \epsilon(a_{1+})$.

Figure 3 shows the charge density [$n(r) \equiv n^+(r) + n^-(r)$] and the spin density [$s(r) \equiv n^+(r) - n^-(r)$] for $\text{Cr}^+(d^5)$, $\text{Cr}^{2+}(d^4)$, and $\text{Cr}^{3+}(d^3)$ impurities. We notice the covalent bonds between the Cr impurity and the neighboring S atoms, which result from hybridization between the Cr 3d orbitals and the host orbitals. The change in the charge density is well localized in the vicinity of the impurity site [Fig. 3(a)]. The dominant contribution to the spin density is induced from the covalently hybridized 3d orbitals at the Cr site. The spin densities integrated over the atomic sphere around the Cr impurity are 3.7 for $\text{Cr}^+(d^5)$, 3.5 for $\text{Cr}^{2+}(d^4)$, and 3.2 for $\text{Cr}^{3+}(d^3)$.

TABLE II. Calculated g values and hyperfine coupling constants for a Cr impurity in ZnS. A is in units of 10^{-4} cm^{-1} .

Charge state	g_{calc}	g_{expt}	A_{calc}	A_{expt}
$\text{Cr}^{3+}(d^3)$	$g = 1.947$		+ 17.1	
$\text{Cr}^{2+}(d^4)$	$g_{\parallel} = 1.930$ $g_{\perp} = 1.960$	$g_{\parallel} = 1.95^a$ $g_{\perp} = 1.98^a$	+ 14.1	
$\text{Cr}^+(d^5)$	$g = 1.999$	$g = 1.9995^{b,c}$	+ 11.9	13.4 ^b

^aReference 23.

^bReference 29.

^cReference 17.

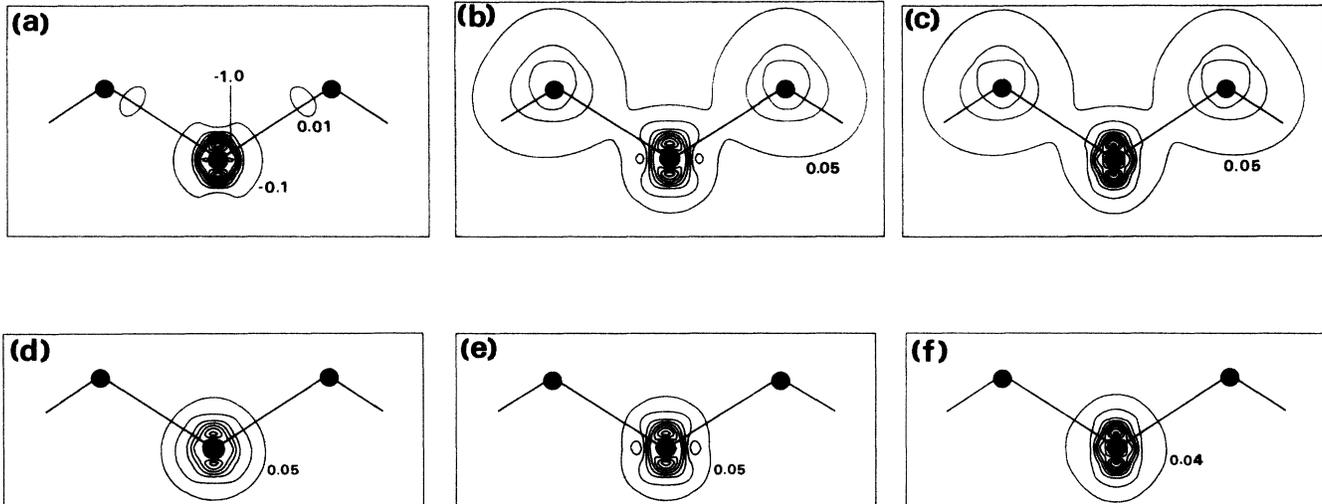


FIG. 3. Contour plot of charge density [(a) Cr^+ , (b) Cr^{2+} , and (c) Cr^{3+}] and spin density [(d) Cr^+ , (e) Cr^{2+} , (f) Cr^{3+}] on the $(1\bar{1}0)$ plane in the vicinity of the impurity. In (a) the charge density is subtracted by the host charge density in ZnS. Contour spacings are 0.3 a.u.^{-3} for (a) and 0.1 a.u.^{-3} for (b)–(f).

We next focus on the hyperfine coupling constant at the impurity site and on the g values. From the present Green's-function calculation, the spin density of valence electrons induced by substituting a Cr impurity for a Zn atom is found to be positively polarized at the impurity nucleus. The $3d$ spin density, in turn, polarizes the core electrons negatively. This core polarization makes the dominant contribution to the hyperfine coupling constant at the Cr impurity site. We have thus performed an all-electron atomic calculation by fixing the valence-electron charge density which is obtained from the Green's-function calculation. The resulting spin densities at the nucleus of the Cr impurity are -0.61 a.u.^{-3} for Cr^{3+} , -0.67 a.u.^{-3} for Cr^{2+} , and -0.71 a.u.^{-3} for Cr^+ , and the calculated hyperfine coupling constants are shown in Table II. The calculated g values²⁸ are also shown in Table II. For the cases of Cr^{2+} and Cr^+ , the

agreement in g values between the present calculation and EPR measurements is reasonable. Yet, no experimental data to be compared with the present calculation are available for Cr^{3+} . The EPR signal of $\text{Cr}^{3+}(d^3)$ could be observed in p -type ZnS, and the experimental confirmation of the present calculation is desirable.

In conclusion, we have performed first-principles Green's-function calculations for a Cr impurity in ZnS for the first time, and clarify the electronic structure and interplay between covalency and ionicity in this potentially important material.

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