Defect properties of $CuCrO_2$: A density functional theory calculation*

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Using the first-principles methods, we study the formation energetics properties of intrinsic defects, and the charge doping properties of extrinsic defects in transparent conducting oxides $CuCrO_2$. Intrinsic defects, some typical acceptor-type, and donor-type extrinsic defects in their relevant charge state are considered. By systematically calculating the formation energies and transition energy, the results of calculation show that, V_{Cu}, O_i, and O_{Cu} are the relevant intrinsic defects in $CuCrO_2$; among these intrinsic defects, V_{Cu} is the most efficient acceptor in $CuCrO_2$. It is found that all the donor-type extrinsic defects have difficulty in inducing n-conductivity in $CuCrO_2$ because of their deep transition energy level. For all the acceptor-type extrinsic defects, substituting Mg for Cr is the most prominent doping acceptor with relative shallow transition energy levels in $CuCrO_2$. Our calculation results are expected to be a guide for preparing promising n-type and p-type materials in $CuCrO_2$.

Keywords: first-principle, defects, formation energy

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1. Introduction

Transparent conducting oxides (TCOs) play an important role in solar cells, flat panel displays, electrochromic mirrors and windows, and other optoelectronic devices.[1] Most of the TCOs such as ZnO[2,3] and SnO_2 have n-type conductivity, in which electrons are the dominant charge carrier. Even so, the application of n-type TCOs is rather restricted if without high merit p-type TCOs because the active functions of many optoelectronic elements come from p–n junctions. In order to construct the transparent p–n junctions devices, it is essential to explore new p-type TCOs so that the combination of the two types of TCOs can be realizable. In 1997, Kawazoe *et al.*[4] first found that transparent thin films of copper–aluminium–oxide $CuAlO_2$ have p-type conductivity. Although the conductivity of $CuAlO_2$ is significantly lower than other n-type conductivity of other TCOs,[5] it still become an important step for the development of transparent p–n junction devices. Delafossite $CuMO_2$ (M = Al, Ga, In, Sc, Y, Cr, rare earths, etc.) have wide band gaps and cation d-domination valence bands, which means they are considered as promising p-type conductivity and have attracted the attention of many researchers.[6−11] These $CuMO_2$ materials present p-type conductivity without intentional doping, and most of the $CuMO_2$ are wide-gap materials in which the value of the band gap excess is 3.1 eV, for example, the optically measured value of the direct band gap of $CuAlO_2$ is about 3.5 eV,[4] and the value of the band gap of $CuGaO_2$ also arrives at 3.6 eV.[12] In the case of $CuCrO_2$, $CuCrO_2$ has been the focus of recent interest as the further p-type TCOs because it still remains tolerably transparent in the visible region.[13] There has been some research[13−15] on $CuCrO_2$, whereas there are still no detailed descriptions about the defect properties of $CuCrO_2$. In particular, we notice that an *ab initio* investigation of defects in $CuCrO_2$ is still lacking. It is well known that properties of semiconductors are mostly determined by intrinsic defects and impurities, thus, it is necessary to understand the mechanism of p-type properties and to design a new doping method for the real-

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ization of more promising p-type $CuCrO_2$. Motivated by this observation, in this study, we report a series of studies on the intrinsic and extrinsic substitutional defects of $CuCrO_2$ by calculating its defect formation energy and transition energy level. It is expected that our present first-principles results will greatly help to explain the various physical properties of defects in $CuCrO_2$ from a microscopic perspective and can be a guide for p-type $CuCrO_2$ material preparation. The rest of this paper is arranged as follows. In Section 2, the computational method is briefly described. In Section 3, we present and discuss our results. Finally, we summarize the conclusions of this work in Section 4.

2. Methods

The total energy calculations in this study are performed by using the first principle projected augmented wave (PAW) pseudopotentials method[16,17] within the local-density approximation (LDA)[18,19] as implemented in the VASP code.[20,21] In our calculation, a supercell containing 48 host atoms is used, and all atomic positions have been relaxed according to the calculated Helmann–Feynman forces. The energy cutoff for the plane-wave basis is 400 eV. The $2 \times 2 \times 2$ Monkhorst–Pack k-point set[22,23] has been used to sample the Brillouin zone. The band structure calculations are performed with a four-atom unit cell, and total energy calculations are performed with a 48-atom supercell. For the charged defects, a jellium background has been added to keep the global charge neutrality of the periodic supercell. We use the projector augmented wave method and the same supercell and same k-point sampling in defect system study in all the calculations. The chemical potentials of elemental solids are obtained from fully converged LDA/PAW total energy calculations. In this study, we substitute group II elements Be, Mg, and Ca, and group IV elements Si, Ge, and Sn one by one for Cu or Cr to introduce extrinsic defects in $CuCrO_2$. In our calculation, the valence electrons include 3d and 4s of Cu, 2s and 2p of O, 5d and 6s of Cr; for the group II elements Be, Ca, and Mg, the valence electrons include 2s of Be, 4s and 4p of Ca, 3s and 3p of Mg; for the group IV elements Si, Ge, and Sn, the valence electrons include 3s and 3p of Si, 4s and 4p of Ge, and 4d, 5s and 5p of Sn.

The crystal structure of the $CuCrO_2$ belongs to the space group of $R\bar{3}m$ (see in Fig. 1). As shown in Fig. 1, one could see that each Cu atom is linearly coordinated with two oxygen atoms to form an O–Cu–O dumbbell unit placed parallel to the c axis. The oxygen atoms that terminate the dumbbells are also each coordinated to three Cr atoms, and the O–Cu–O dumbbell layers in a hexagonal plane are separated by a CrO_6 edge-sharing octahedral layer. The structure is defined by three crystallographic parameters: two lattice parameters, a, c, and the internal parameter, u. In the primitive cell, one Cu atom is located at $(0,0,0)$, one Cr atom is located at $(0,0,0.5)$, and two O atoms at $\pm(0,0,u)$. All the lattice parameters are fitting to the Murnaghan equation of state[24] based on the LDA calculations, to $CuCrO_2$, the calculated structural parameters are $a = 2.933$ (2.973) Å (1 Å = 0.1 nm), $c = 17.016$ (17.100) Å, $c/a = 5.802$ (5.752) Å, and $u = 0.1072$ (0.1079) Å; compared with the available experimental data[25] in parentheses.

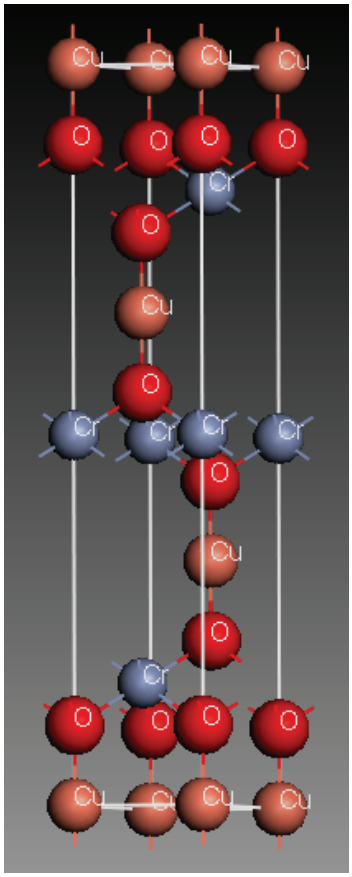


Fig. 1. (colour online) The crystal structure of the $CuCrO_2$. The red atoms are O atoms, the brown atoms are Cu atoms, and the purple atoms are Cr atoms.

In order to improve and control p-type conductivity of $CuCrO_2$, we study which kind of intrinsic defects is favorable. For this purpose, we calculate the formation energy and defect transition energy levels of defects in $CuCrO_2$. According to notation of

formation energy,[26] the defect formation energy depends sensitively on the atomic chemical potential as well as on the electron Fermi energy

$$\Delta H_{\rm f}(\alpha,q) = \Delta E(\alpha,q) + n_{\rm Cu}\mu_{\rm Cu} + n_{\rm O}\mu_{\rm O} + n_{\rm Cr}\mu_{\rm Cr} + n_{\rm A}\mu_{\rm A} + qE_{\rm F}, \quad (1)$$

where

$$\Delta E(\alpha,q) = E(\alpha,q) - E_0({\rm CuCrO_2}) + n_{\rm Cu}\mu^0_{\rm Cu} + n_{\rm O}\mu^0_{\rm O} + n_{\rm Cr}\mu^0_{\rm Cr} + n{\rm A}\mu^0_{\rm A} + qE_{\rm VBM}. \quad (2)$$

Here $E(\alpha,q)$ is the total energy of the supercell containing the defect α in charge state q. $E_0({\rm CuCrO_2})$ is the total energy of the same supercell free of any defect. $n_{\rm Cu}$, $n_{\rm O}$, $n_{\rm Cr}$, and $n_{\rm A}$ are the number of Cu, O, Cr, and dopants transferred from the supercell to the reservoirs in forming the defect cell, and q is the number of electrons which transferred from the supercell to the reservoirs in forming the defect cell. $\mu^0_{\rm Cu}$, $\mu^0_{\rm Cr}$, $\mu^0_{\rm A}$, $\mu^0_{\rm O}$ are the standard chemical potentials, or the total energy of ground-state solid Cu (fcc), Cr (fcc), dopant atom, and O (oxygen). $E_{\rm F}$ is the Fermi energy measured from the valence band maximum (VBM) $E_{\rm VBM}$. $E_{\rm F}$ is bound between $E_{\rm VBM}$ and $E_{\rm CBM}$.

The defect transition energy level $\varepsilon_\alpha(q/q')$ is defined as the value of the Fermi level where the formation energy of q equals that of q', i.e.,

$$\varepsilon_\alpha(q/q') = [\Delta E(\alpha,q) - \Delta E(\alpha,q')]/(q'-q). \quad (3)$$

There are some thermodynamic limits on chemical potentials that depend on the experimental growth conditions. For $\rm CuCrO_2$, the range of the chemical potentials can be determined by considering several factors listed below.

(i) The values that will cause precipitation of solid elemental Cu, Cr, O, and the dopant A, so that

$$\mu_{\rm Cu} \le 0, \quad \mu_{\rm Cr} \le 0, \quad \mu_{\rm O} \le 0, \quad \mu_{\rm A} \le 0; \quad (4)$$

(ii) By the values that maintain a stable $\rm CuCrO_2$ compound, so that

$$\mu_{\rm Cu} + \mu_{\rm Cr} + 2\mu_{\rm O} = \Delta H_{\rm f}({\rm CuCrO_2}), \quad (5)$$

where $\Delta H_{\rm f}({\rm CuCrO_2}) = -5.11$ eV is the calculated formation energy of solid $\rm CuCrO_2$.

(iii) By the values that will cause formation of binaries, so that

$$n\mu_{\rm A} + m\mu_{\rm O} \le \Delta H_{\rm f}({\rm A}_n{\rm O}_m),$$
$$2\mu{\rm Cr} + 3\mu_{\rm O} \le \Delta H_{\rm f}({\rm Cr_2O_3}),$$
$$2\mu_{\rm Cu} + \mu_{\rm O} \le \Delta H_{\rm f}({\rm Cu_2O}), \quad (6)$$

where the calculated $\Delta H_{\rm f}({\rm Cr_2O_3}) = -9.55$ eV, $\Delta H_{\rm f}({\rm Cu_2O}) = -1.41$ eV. For $\rm CuCrO_2$, the chemical potential ranges of the three components can be determined as follows: $-0.71 \le \mu_{\rm Cu} \le 0$, $-1.41 \le \mu_{\rm O} \le 0$, $-5.58 \le \mu_{\rm Cr} \le -3.47$.

3. Results and discussion

Table 1 lists the calculated formation energies of the acceptor-type intrinsic defects in terms of $\Delta E(\alpha,q)$ in Eq. (2) and defect transition levels $\varepsilon_\alpha(q/q')$ of Eq. (3). One can find in Table 1 that intrinsic defects $\rm V_{Cu}$, $\rm O_i$, and $\rm O_{Cu}$, under the condition $q=0$, the formation energies $\Delta H_{\rm f}$ ($\rm V_{Cu}$), $\Delta H_{\rm f}$ ($\rm O_i$), and $\Delta H_{\rm f}$ ($\rm O_{Cu}$) were -1.69, -2.19, and -0.89 eV, respectively, which means these defects can occur in $\rm CuCrO_2$. In addition, considering the transition energy level position, the calculated result shows that $\rm V_{Cu}$, $\rm O_i$, and $\rm O_{Cu}$ have transition energy levels $(-/0)$ at 0.83, 1.25, and 1.03 eV above the VBM, respectively. The transition energy level is crucial for carrier concentration. A high transition energy level indicates that this kind of defect would not be an important dopant while a low level indicates the opposite.

To obtain a more precise knowledge of intrinsic defect properties in $\rm CuCrO_2$, we have plotted the formation energy map (Fermi energy and chemical potential dependencies of the defect formation energies listed in Table 1 are shown graphically in Fig. 2). We mainly consider the trend of formation energies under the O-rich and O-poor conditions, and $E_{\rm F}$ is bound between $E_{\rm VBM}$, and $E_{\rm CBM}$, whose difference gives the band gap. From Fig. 2 and the data in Table 1, we derive the formation energies of charged defects. When Fermi level $E_{\rm F}$ moves toward CBM, according to Eq. (1), the formation energies of acceptor-type defects will decrease, while the formation energy of donor energy defects will increase. Take the formation energy of $\rm Cu_{Cr}$ under O-poor condition for example, when $E_{\rm F}$ is located at VBM, the formation energy $\Delta H_{\rm f}$ ($\rm Cu_{Cr}$) is 1.8 eV, which means it is difficult for $\rm Cu_{Cr}$ to form in $\rm CuCrO_2$. When the $E_{\rm F}$ moves toward CBM, the formation energy $\Delta H_{\rm f}$ ($\rm Cu_{Cr}$) decreases, in particular, when the value of $E_{\rm F}$ arrives at 2.2 eV above the VBM, $\Delta H_{\rm f}$ ($\rm Cu_{Cr}$) begins to become negative, which means $\rm Cu_{Cr}$ would be spontaneous formation in $\rm CuCrO_2$ when the value of $E_{\rm F} \ge 2.2$ eV above the VBM. One can also find from Fig. 2 that, $\rm V_{Cu}$, $\rm O_i$, and $\rm O_{Cu}$ are the relevant intrinsic defects in

both O-rich and O-poor conditions in $CuCrO_2$; in addition, V_{Cr} can be formed with the increasing value of E_F. Acceptor-type intrinsic defect O_{Cr} hardly occurs in $CuCrO_2$ because of high formation energies. From these calculated results about transition energy levels, one can find that the defect V_{Cu} could relatively easily introduce negative charge in $CuCrO_2$ because V_{Cu} has the shallowest transition energy level.

Table 1. For $CuCrO_2$, the acceptor-type intrinsic defect formation energies in terms of $\Delta E(\alpha, q)$ in Eq. (2) and defect transition levels $\varepsilon_\alpha(q/q')$ of Eq. (3). The n_{Cu}, n_{Cr}, and n_O are the numbers of Cu, Cr, and O atoms, and q are the numbers of excess electrons, transferred from the defect-free crystal to the reservoirs to form one defect.

Defect α	$\Delta E(\alpha, q)$/eV	n_{Cu}	n_{Cr}	n_O	q
V_{Cu}^{0}	−1.69	+1	0	0	0
V_{Cu}^{-}	−0.86	+1	0	0	−1
Defect transition level: $(-/0) = Ev + 0.83$ eV					
V_{Cr}^{0}	1.87	0	+1	0	0
V_{Cr}^{-}	2.55	0	+1	0	−1
V_{Cr}^{2-}	3.38	0	+1	0	−2
V_{Cr}^{3-}	4.38	0	+1	0	−3
Defect transition level: $(-/0) = Ev + 0.68$ eV, $(2-/-) = Ev + 0.83$ eV, $(3-/2-) = Ev + 1.0$ eV					
O_{Cr}^{0}	6.41	0	+1	−1	0
O_{Cr}^{-}	7.44	0	+1	−1	−1
O_{Cr}^{2-}	9.39	0	+1	−1	−2
Defect transition level: $(-/0) = Ev + 1.03$ eV, $(2-/-) = Ev + 1.95$ eV					
Cu_{Cr}^{0}	1.8	−1	+1	0	0
Cu_{Cr}^{-}	3.04	−1	+1	0	−1
Cu_{Cr}^{2-}	4.39	−1	+1	0	−2
Defect transition level: $(-/0) = Ev + 1.24$ eV, $(2-/-) = Ev + 1.35$ eV					
O_{i}^{0}	−2.19	0	0	−1	0
O_{i}^{-}	−0.94	0	0	−1	−1
O_{i}^{2-}	0.48	0	0	−1	−2
Defect transition level: $(-/0) = Ev + 1.25$ eV, $(2-/-) = Ev + 1.42$ eV					
O_{Cu}^{0}	−0.89	+1	0	−1	0
O_{Cu}^{-}	0.14	+1	0	−1	−1
O_{Cu}^{2-}	1.3	+1	0	−1	−2
Defect transition level: $(-/0) = Ev + 1.03$ eV, $(2-/-) = Ev + 1.16$ eV					

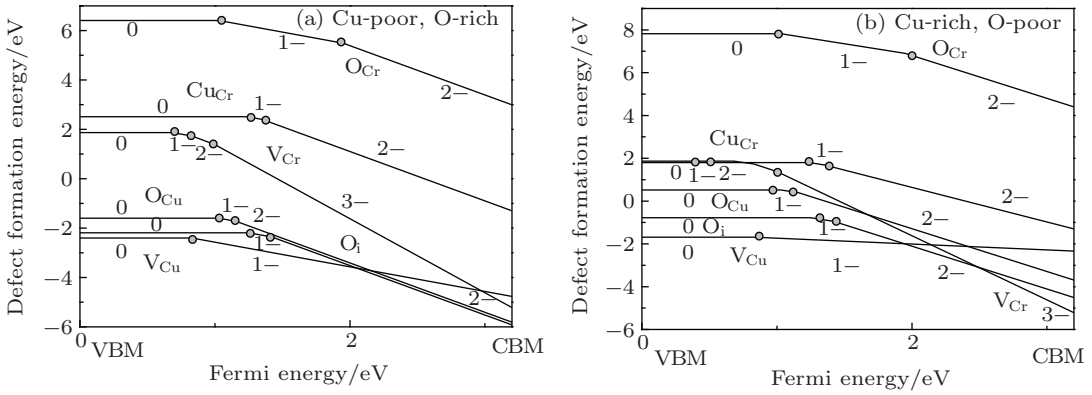


Fig. 2. The formation energy as a function of Fermi level for acceptor-type defects under O-rich (a) and O-poor (b) conditions in $CuCrO_2$. The zero of Fermi energy is set to E_{VBM}. Charge state q determines the slope of each line segment. Solid dots denote values of formation energy E_f where transition between charge states occurs.

Table 2 lists the calculated formation energies of the donor-type intrinsic defects in terms of $\Delta E(\alpha, q)$ in Eq. (2) and defect transition levels $\varepsilon_\alpha(q/q')$ of Eq. (3). It is revealed in Table 2 that, all kinds of donor-type

intrinsic defects have the high formation energy and deep transition energy levels in $CuCrO_2$, thus without the intension doping, $CuCrO_2$ have no n-type conductivity.

Table 2. For $CuCrO_2$, the donor-type intrinsic defect formation energies are in terms of $\Delta E(\alpha, q)$ in Eq. (2) and defect transition levels $\varepsilon_\alpha(q/q')$ in Eq. (3). The $n_{\rm Cu}$, $n_{\rm Cr}$, and $n_{\rm O}$ are the numbers of Cu, Cr, and O atoms, and q are the numbers of excess electrons, transferred from the defect-free crystal to the reservoirs to form one defect.

Defect α	$\Delta E(\alpha, q)$/eV	$n_{\rm Cu}$	$n_{\rm Cr}$	$n_{\rm O}$	q
$V_{\rm O}^{0}$	3.01	0	0	+1	0
$V_{\rm O}^{+}$	2.19	0	0	+1	+1
$V_{\rm O}^{2+}$	1.44	0	0	+1	+2
Defect transition level: $(0/+) = Ec - 2.38$ eV, $(+/2+) = Ec - 2.45$ eV					
$Cr_{\rm Cu}^{0}$	3.55	+1	−1	0	0
$Cr_{\rm Cu}^{+}$	2.2	+1	−1	0	+1
$Cr_{\rm Cu}^{2+}$	0.95	+1	−1	0	+2
Defect transition level: $(0/+) = Ec - 1.85$ eV, $(+/2+) = Ec - 1.95$ eV					
$Cu_{\rm i}^{0}$	2.63	−1	0	0	0
$Cu_{\rm i}^{+}$	1.08	−1	0	0	+1
Defect transition level: $(0/+) = Ec - 1.65$ eV					
$Cr_{\rm i}^{0}$	5.83	0	−1	0	0
$Cr_{\rm i}^{+}$	4.18	0	−1	0	+1
$Cr_{\rm i}^{2+}$	2.67	0	−1	0	+2
$Cr_{\rm i}^{3+}$	1.24	0	−1	0	+3
Defect transition level: $(0/+) = Ec - 1.55$ eV, $(+/2+) = Ec - 1.69$ eV, $(2+/3+) = Ec - 1.77$ eV					
$Cr_{\rm O}^{0}$	7.37	0	−1	+1	0
$Cr_{\rm O}^{+}$	6.08	0	−1	+1	+1
$Cr_{\rm O}^{2+}$	4.91	0	−1	+1	+2
$Cr_{\rm O}^{3+}$	3.92	0	−1	+1	+3
Defect transition level: $(0/+) = Ec - 1.91$ eV, $(+/2+) = Ec - 2.03$ eV, $(2+/3+) = Ec - 2.21$ eV					
$Cu_{\rm O}^{0}$	6.44	−1	0	+1	0
$Cu_{\rm O}^{+}$	5.09	−1	0	+1	+1
$Cu_{\rm O}^{2+}$	4.03	−1	0	+1	+2
$Cu_{\rm O}^{3+}$	3.08	−1	0	+1	+3
Defect transition level: $(0/+) = Ec - 1.85$ eV, $(+/2+) = Ec - 2.14$ eV, $(2+/3+) = Ec - 2.25$ eV					

From these intrinsic calculated results, it is clearly seen that $V_{\rm Cu}$ is the most prominent intrinsic acceptor for $CuCrO_2$. However, the transition energy levels of $V_{\rm Cu}$ are still too high to reach high hole density at room temperature. Remarkably, this result can be used to explain why the p-type conductivity of $CuCrO_2$ is low at room temperature.[27] In order to obtain a more precise knowledge of defects and design a highly efficient p-type $CuCrO_2$, we investigate all of the possible acceptor-type dopant atoms in $CuCrO_2$ based on the first-principle electronic structure calculations. In an extrinsic defect study, one can predict whether a dopant atom is a donor or an acceptor by simply counting the number of the valence electrons of the dopant atoms and the host elements atoms. In $CuCrO_2$, Cu is a monovalent cation and Cr is a trivalent cation, thus one can expect that substituting the group II elements for Cu introduces acceptors; substituting the group IV elements for both Cu and Cr introduces donors. Table 3 lists the calculated formation energies $\Delta E(\alpha, q)$ of the dopants in a neutral charge state and at $\mu_{\rm i} = 0$ in Eq. (1). From the calculated results, for the donor-type extrinsic defects, only $Sn_{\rm Cr}$ defects have positive formation energy 2.29 eV, which means Sn atoms are very difficult to substitute for Cr atoms. Comparing with $Sn_{\rm Cr}$, other donor-type defects have negative formation energy, which means these defects occur very easily in $CuCrO_2$. Figure 3 presents the calculated transition energy levels of the extrinsic defects in $CuCrO_2$. As shown in Fig. 3, one could find that all the donor-type extrinsic defects have deep transition energy. This means that all the donor extrinsic defects have great difficulty in introducing the positive charge in $CuCrO_2$,

which means it is difficult for these dopant atoms to induce n-conductivity in $CuCrO_2$. For A_{Cr} (A = Be, Ca , Mg) acceptor-type extrinsic defects, the calculated results show that these acceptor-type extrinsic defects have negative formation energy, which means all acceptor-type extrinsic defects can be formed spontaneously in $CuCrO_2$. In addition, considering the transition energy level position, Be_{Cr}, Ca_{Cr}, and Mg_{Cr} have transition energy levels $(-/0)$ at 0.81, 1.06, and 0.31 eV above the VBM, respectively. Among these extrinsic defects, Mg_{Cr} has the shallowest transition energy (0.31 eV). According to Nagarajan's study,[15] Mg-doped has the excellent reported p-type conduction of $CuCrO_2$. Our calculated results also show that, Mg_{Cr} are the most prominent acceptors for $CuCrO_2$, which is consistent with previous result.[15] Based on our calculated results and discussion mentioned above, in order to increase p-type conductivity in $CuCrO_2$, we could substitute Mg atoms for Cr atoms by the sit-selective doping method through atomic layer epitaxy growth, which could be realized by controlling Cr-vapor pressure as well as controlling copper partial pressure in the MBE or MOCVD crystal growth process.

Table 3. The calculated formation energies $\Delta E(\alpha, q)$ [Eq. (1)] of dopants at neutral charge state ($q = 0$) and $\mu_i = 0$.

Defect α	$\Delta E(\alpha, q)$/eV	Defect α	$\Delta E(\alpha, q)$/eV
Be_{Cr}	−1.24	Be_{Cu}	−1.45
Ca_{Cr}	−0.54	Ca_{Cu}	−1.56
Mg_{Cr}	−2.13	Mg_{Cu}	−1.50
Si_{Cr}	−3.87	Si_{Cu}	−1.93
Ge_{Cr}	−0.10	Ge_{Cu}	−1.26
Sn_{Cr}	2.29	Sn_{Cu}	−0.75

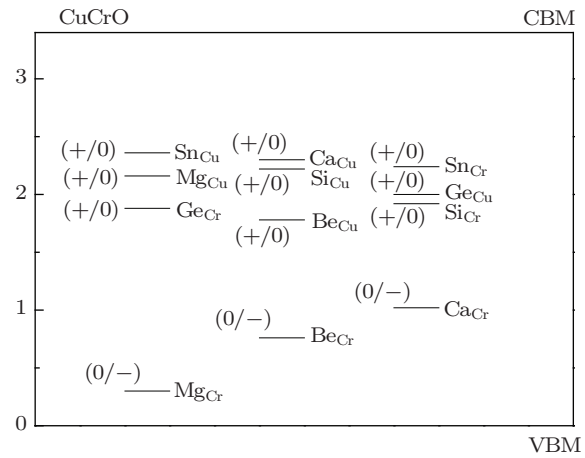


Fig. 3. The calculated transition energy levels of the extrinsic defects in $CuCrO_2$.

4. Summary

In summary, we have studied the formation energies and transition energy levels of intrinsic and extrinsic defects in $CuCrO_2$ through the first-principles calculations. For intrinsic defect study, the calculated results show that, V_{Cu}, O_i, and O_{Cu} are the relevant native defects in $CuCrO_2$, and among these defects, Cu vacancy could be the most prominent native acceptor with the shallowest transition energy level. In studying the extrinsic defect properties of $CuCrO_2$, by choosing some typical group II elements and group IV elements as dopant atoms, the formation energies and transition energy levels of donor-type and acceptor-type extrinsic defects were calculated for improving conductivity in $CuCrO_2$. Based upon the calculated results, we proposed a new valence control method for the fabrication of p-type $CuCrO_2$: doping with an Mg acceptor for the Cr atoms, site-selectively, with decreasing O-vapor pressure and increasing Cu-vapor pressure during the thermal nonequilibrium crystal-growth method such as the PLD, MBE or MOCVD method. For the n-type property in $CuCrO_2$, it is difficult for donor-type extrinsic defects to induce n-conductivity in $CuCrO_2$ because of their deep transition energy level. We hope our calculated results serve as guidance for obtaining promising p-type conductivity in $CuCrO_2$.

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