

Self-consistent electronic structures of magnetic semiconductors by a discrete variational $X\alpha$ calculation. I. Ferromagnetic spinels, CdCr_2S_4 and CdCr_2Se_4

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The electronic band structures of ferromagnetic CdCr_2S_4 and CdCr_2Se_4 are self-consistently calculated by using the discrete variational $X\alpha$ method. The general features of the band structures are quite similar between sulfide and selenide; each structure consists of relatively narrow valence bands, fairly wide conduction bands, and very narrow d bands. The $3de$ and $3d\gamma$ bands for up spin lie in the energy region near the top of the valence bands and around the bottom of the lowest conduction band, respectively, and both d bands for down spin fall in the conduction bands. The maximum point of the valence bands has Σ_4 symmetry for both compounds, and the minimum point of the conduction band has A_1 for sulfide and Γ_1 for selenide. The fundamental energy gap at the Γ point is 2.6 eV for sulfide and 2.3 eV for selenide. The spin polarization of the $3d$ orbitals of Cr is about 3.5, in which 0.5 comes from the $3d\gamma$ components mixed with the valence bands, while the spin polarization of the outermost p orbitals of chalcogen ion has the opposite sign, the magnitude of which is about 0.3.

I. INTRODUCTION

Chromium spinels CdCr_2S_4 and CdCr_2Se_4 are typical ferromagnetic semiconductors. Their space group is Oh^7 (Ref. 1). Their optical, electrical, and magnetic properties have been investigated extensively. In the previous paper² (hereafter called I), we calculated the electronic band structures of CdCr_2S_4 and CdCr_2Se_4 using the extended Hückel theory (EHT) and compared the results with the optical experiments. It has been shown that the absorption edge red-shifting with decreasing temperature is assigned to the transition from the $3de$ band to the lowest conduction band which consists mainly of the $4s$ orbitals of Cr, and that the red-shift of the absorption edge is interpreted in terms of the exchange splitting of the lowest conduction band. The parameters included in the calculation have been determined semiempirically. A nonempirical calculation of the electronic structure without adjustable parameters is desired for full understanding of the physical properties of the chromium spinels.

In the present paper, we calculate the electronic band structure of CdCr_2S_4 and CdCr_2Se_4 in the ferromagnetic phase using the discrete variational-(DV) $X\alpha$ method.³⁻⁵ The DV- $X\alpha$ method, based on the Hartree-Fock-Slater model, has been used for various molecules and solids with reasonable results. In the DV- $X\alpha$ method the matrix elements are evaluated as weighted sums of the values determined at discrete sample points. The resulting advantage is that we can choose any type of basis set and any crystal potential without the difficulty of many-center integration appearing in the standard LCAO (linear-combination-of-

atomic-orbitals) scheme. Spin-polarized self-consistent calculations have rarely been done on such a large system as CdCr_2S_4 and CdCr_2Se_4 without any restriction on the crystal potential.

II. PROCEDURE OF CALCULATION

The one-electron Hamiltonian is written (in atomic units) as

$$H = -\frac{1}{2}\nabla^2 + V^\sigma(\vec{r}). \quad (1)$$

Here, the superscript σ denotes electron spin and the crystal potential $V^\sigma(\vec{r})$ consists of the following two terms, Coulomb and exchange correlation:

$$V_c(\vec{r}) = -\sum_{m\nu} \frac{Z_\nu}{|\vec{r} - \vec{r}_\nu - \vec{R}_m|} + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}', \quad (2)$$

$$V_x^\sigma(\vec{r}) = -3\alpha \left(\frac{3}{4\pi} \rho^\sigma(\vec{r}) \right)^{1/3}, \quad (3)$$

where \vec{R}_m and \vec{r}_ν denote the position vectors of m th unit cell and ν th atomic site in the unit cell, respectively, Z_ν is the atomic number (nucleus charge) of ν th atom,

$$\rho(\vec{r}) = \sum_\sigma \rho^\sigma(\vec{r}), \quad (4)$$

and α is the exchange scaling parameter. We take 0.7 for the scaling parameter in this calculation.

The charge distribution of σ -spin electron $\rho^\sigma(\vec{r})$ is approximated as a superposition of spherical atomic charge distributions $\rho_\nu^\sigma(r)$:

$$\rho^\sigma(\vec{r}) = \sum_{m\nu} \rho_\nu^\sigma(|\vec{r} - \vec{r}_\nu - \vec{R}_m|). \quad (5)$$

The spherical atomic charge distribution is given as

$$\rho_\nu^\sigma(r) = \frac{1}{4\pi} \sum_{nl} f_{\nu nl}^\sigma [R_{\nu nl}^\sigma(r)]^2, \quad (6)$$

where $f_{\nu nl}^\sigma$ and $R_{\nu nl}^\sigma(r)$ are the occupation number and the radial function of ($nl\sigma$) orbital of ν th atom, respectively. The radial functions are self-consistently calculated by numerical integration of the central-field atomic one-electron equation,

$$\left[-\frac{1}{2}\nabla^2 - \frac{Z_\nu}{r} + \sum_\sigma \int \frac{\rho_\nu^\sigma(r')}{|\vec{r} - \vec{r}'|} d\vec{r}' - 3\alpha \left(\frac{3}{4\pi} \rho_\nu^\sigma(r) \right)^{1/3} + A_\nu(r) \right] \chi_{\nu lm}^\sigma(\vec{r}) = \epsilon_{\nu lm}^\sigma \chi_{\nu lm}^\sigma(\vec{r}), \quad (7)$$

$$\chi_{\nu lm}^\sigma(\vec{r}) = R_{\nu nl}^\sigma(r) Y_{lm}(\hat{r}), \quad (8)$$

where $\epsilon_{\nu lm}^\sigma$ are the orbital energy eigenvalues and $Y_{lm}(\hat{r})$ are the spherical harmonics. The additional term $A_\nu(r)$, nonzero only for negative ions, is the external well potential to get a bound solution for the virtual states. For both S and Se ions we use

$$A(r) = -2.0 \text{ a.u. for } r < 6.0 \text{ a.u.} \quad (9)$$

In order to get a fast convergence of lattice sums in Eq. (2), the Coulomb potential is divided into the two terms, long range and short range:

$$V_C(\vec{r}) = V_{\text{LRC}}(\vec{r}) + V_{\text{SRC}}(\vec{r}), \quad (10)$$

$$V_{\text{LRC}}(\vec{r}) = - \sum_{m\nu} \frac{Q_\nu}{|\vec{r} - \vec{r}_\nu - \vec{R}_m|}, \quad (11)$$

$$V_{\text{SRC}}(\vec{r}) = \sum_{m\nu} \left(v_C^\nu(\vec{r} - \vec{r}_\nu - \vec{R}_m) + \frac{Q_\nu}{|\vec{r} - \vec{r}_\nu - \vec{R}_m|} \right), \quad (12)$$

where

$$Q_\nu = Z_\nu - \sum_{nl\sigma} f_{\nu nl}^\sigma, \quad (13)$$

$$v_C^\nu(\vec{r}) = - \frac{Z_\nu}{|\vec{r}|} + \sum_\sigma \int \frac{\rho_\nu^\sigma(r')}{|\vec{r} - \vec{r}'|} d\vec{r}'. \quad (14)$$

The long-range term $V_{\text{LRC}}(\vec{r})$ is evaluated by using Evjen's procedure⁶ throughout the neutral cubic supercell centered at r , which consists of 216 molecules. The lattice sums in Eqs. (5) and (12) are carried out for $|\vec{r} - \vec{r}_\nu - \vec{R}_m| \leq 20$ a.u. Then, the error in $V_C(\vec{r})$ is less than 10^{-3} a.u.

The λ th eigenfunction for σ -spin electron $\psi_\lambda^\sigma(\vec{k}, \vec{r})$ is represented as

$$\psi_\lambda^\sigma(\vec{k}, \vec{r}) = \sum_{\nu p} C_{\nu p, \lambda}^{\vec{k}, \sigma} \phi_{\nu p}^\sigma(\vec{k}, \vec{r}). \quad (15)$$

The Bloch basis functions $\phi_{\nu p}^\sigma(\vec{k}, \vec{r})$ are given in the LCAO scheme as

$$\phi_{\nu p}^\sigma(\vec{k}, \vec{r}) = L^{-1/2} N_{\nu p}^{\vec{k}, \sigma} \sum_m e^{i\vec{k} \cdot \vec{R}_m} \chi_{\nu p}^\sigma(\vec{r} - \vec{r}_\nu - \vec{R}_m), \quad (16)$$

where $N_{\nu p}^{\vec{k}, \sigma}$ is the normalization constant and the subscript p stands for nl . The atomic orbitals $\chi_{\nu p}^\sigma(\vec{r})$ are numerically generated by solving Eq. (7). We use the following atomic orbitals in a numerical form as the basis set: $1s-5p$ for Cd, $1s-4p$ for Cr, $1s-3p$ for S, and $1s-4p$ for Se.

The discrete-variational procedure leads to the secular equation

$$\underline{HC} = \underline{SCE}, \quad (17)$$

in which the matrix elements are evaluated as weighted sums of the integrand values determined at sample points:

$$H_{ij} = \sum_l w(\vec{r}_l) \phi_i^*(\vec{r}_l) [H \phi_j(\vec{r})]_{\vec{r}=\vec{r}_l}, \quad (18)$$

$$S_{ij} = \sum_l w(\vec{r}_l) \phi_i^*(\vec{r}_l) \phi_j(\vec{r}_l), \quad (19)$$

where the subscripts i and j stand for ($\nu p \sigma$). The integration weight $w(\vec{r}_l)$ at the l th sample point is determined from an appropriate distribution function $D(\vec{r}_l)$ of the sample points, that is,

$$w(\vec{r}_l) = \frac{1}{ND(\vec{r}_l)}, \quad (20)$$

where N is the total number of sample points. A superposition of Fermi-type functions⁷ centered at each atomic site is used as the distribution function

$$D(\vec{r}) = \sum_{m\nu} t_\nu d_\nu(|\vec{r} - \vec{r}_\nu - \vec{R}_m|), \quad (21)$$

where

$$d_\nu(r) = \frac{A_\nu}{4\pi r^2 \{1 + \exp[\beta_\nu(r - R_0^\nu)]\}}. \quad (22)$$

In our calculation, a total of 3000 sample points in a unit cell is enough to get the occupied band energies to an accuracy within 0.2 eV. In order to reduce the dimension of the matrix in the secular equation (17), the core states are frozen⁸ and the valence-state basis functions are orthogonalized to the core states.

The Mulliken population analysis⁹ is applied to the eigenfunctions. The population for the ($nl\sigma$) shell of the ν th atom is defined by

$$f_{\nu nl}^\sigma = \frac{N\Omega}{(2\pi)^3} \int d\vec{k} \sum_\lambda t_{\nu nl, \lambda}^{\vec{k}, \sigma}, \quad (23)$$

where

$$t_{vni,\lambda}^{\vec{k},\sigma} = \sum_{i \in \{vni\sigma\}} \sum_j C_{i\lambda}^{\vec{k},\sigma*} C_{j\lambda}^{\vec{k},\sigma} S_{ij}. \quad (24)$$

We apply again the sampling integration to the \vec{k} -space integral of Eq. (23),

$$f_{vni}^{\sigma} = \sum_k w_k \sum_{\lambda} t_{vni,\lambda}^{\vec{k},\sigma}. \quad (25)$$

The \vec{k} dependence of the integrand in Eq. (23) is relatively weak as shown in Fig. 1. As the sample k points Γ , X , and L are selected and relative values of their weights w_k are 1, 3, and 4, respectively, the self-consistent charge procedure¹⁰ is adopted: The self-consistency criterion is the coincidence between input and output population in Eqs. (6) and (23), respectively. Only a few iterations are required to attain the coincidence within 0.02.

III. RESULTS

The calculated band structures of CdCr_2S_4 and CdCr_2Se_4 , up-spin and down-spin bands, in the ferromagnetic phase, are shown along some symmetry lines of the Brillouin zone in Figs. 2 and 3, respectively. As seen in these figures, the general features of the band structures are quite similar between the sulfide and selenide; each structure consists of relatively narrow valence bands, fairly wide conduction bands, and very narrow d bands. The up-spin and down-spin bands have essentially the same dispersion, but the position of the $3d$ bands of Cr, relative to the valence and conduction bands, are quite different between the

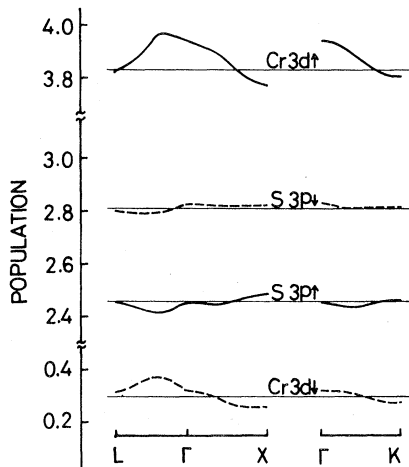


FIG. 1. Dispersion of the Mulliken charge population in CdCr_2S_4 across the Brillouin zone. Horizontal lines indicate k -averaged values. The populations for other orbitals are omitted since their dispersions are much weaker.

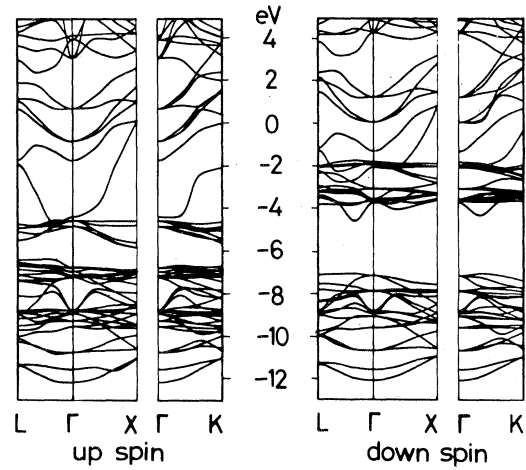


FIG. 2. Calculated band structure of CdCr_2S_4 .

up and down spins, and especially the $3d\epsilon$ bands of up spin below the Fermi energy, as expected for the Cr^{3+} ion in an octahedral crystalline field.

The energies of various levels and the contents of their wave functions at the Γ point are listed in Tables I and II for either spins and for the sulfide and selenide. It can be seen from those tables that the highest level of the valence bands is composed of the almost pure p orbitals of anion. The $3d\epsilon$ orbitals of Cr do not mix with other orbitals at all (at the Γ point), and the levels arising from the $3d\epsilon$ orbitals of Cr lie in the energy range near the top of the valence bands for up spin and around the bottom of the conduction bands for down spin. The bottom of the conduction bands is composed mainly of the $4s$ orbital of Cr with large mixing with the $5s$ of Cd. The level composed of the $5s$ of Cd and $4p$ of Cr lies immediately above the

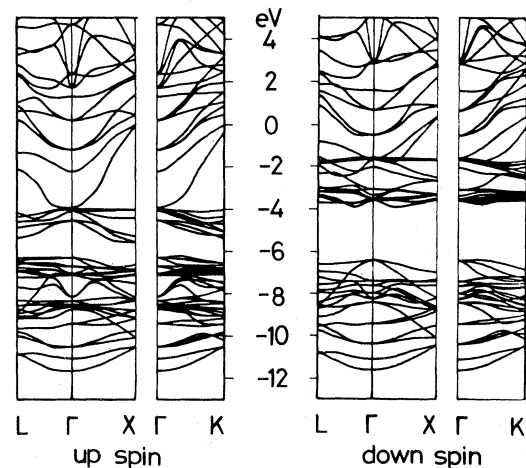


FIG. 3. Calculated band structure of CdCr_2Se_4 .

TABLE I. Atomic-orbital populations for (a) up-spin and (b) down-spin eigenfunctions of CdCr_2S_4 at the Γ point. The figure 0.00 means less than 0.005 and the blank means exactly zero by symmetry. The abbreviated notations for the eigenfunctions, Lc and Hv , mean the lowest conduction band and the highest valence band, respectively, and other notations, $A(d\gamma-p)$ and $B(d\gamma-p)$, mean the antibonding and bonding states of the chromium $3d\gamma$ and sulfur $3p$ orbitals, respectively.

Symmetry	E (eV)	Cd 5s	Cd 5p	Cr 3d	Cr 4s	Cr 4s	S 3p
(a) up spin							
1, c	4.15	0.70		0.00	0.22		0.08
15, c	3.96		0.25			0.73	0.02
25, c	3.10					1.03	-0.03
15, c	0.69		0.14			0.85	0.01
25', c	-0.86		0.33	0.00	0.63		0.04
2', c	-1.76	0.39				0.62	0.00
1, Lc	-4.41	0.26		0.00	0.72		0.01
12, $A(d\gamma-p)$	-4.59			0.44			0.56
15', $A(d\gamma-p)$	-4.60			0.47			0.53
25', $A(d\gamma-p)$	-4.86		0.00	0.65	0.00		0.36
1, $d\epsilon$	-6.76	0.00		1.00	0.00		0.00
12, $d\epsilon$	-6.79			1.00			0.00
15, Hv	-6.96		0.00			0.03	0.97
25', $d\epsilon$	-7.14		0.00	1.00	0.00		0.00
15', $d\epsilon$	-7.19			1.00			0.00
25', $d\epsilon$	-7.24		0.00	1.00	0.00		0.00
15', $B(d\gamma-p)$	-8.77			0.53			0.47
25, v	-8.77					-0.03	1.03
12, $B(d\gamma-p)$	-8.84			0.56			0.44
15, v	-8.94		0.02			0.04	0.94
25', $B(d\gamma-p)$	-9.27		0.00	0.35	0.01		0.64
12', v	-9.54					0.00	1.00
25', v	-10.76		0.00	0.01	0.08		0.91
2', v	-11.56	0.03				0.02	0.95
1, v	-12.16	0.03		0.00	0.06		0.91
(b) down spin							
15, c	4.87		0.34			0.65	0.01
25, c	4.32					1.04	-0.04
1, c	4.25	0.67		0.00	0.28		0.05
15, c	1.22		0.18			0.82	0.00
25', c	0.04		0.41	0.00	0.58		0.01
2', c	-1.36	0.42				0.59	0.00
25', $A(d\gamma-p)$	-1.86		0.00	0.88	0.00		0.12
15', $A(d\gamma-p)$	-2.00			0.82			0.18
12, $A(d\gamma-p)$	-2.12			0.80			0.20
1, $d\epsilon$	-3.12	0.00		1.00	0.00		0.00
12, $d\epsilon$	-3.13			1.00			0.00
25', $d\epsilon$	-3.60		0.00	1.00	0.00		0.00
15', $d\epsilon$	-3.63			1.00			0.00
25', $d\epsilon$	-3.70		0.00	1.00	0.00		0.00
1, Lc	-3.78	0.29		0.00	0.70		0.00
15, Hv	-7.17		0.00			0.01	0.99
12, $B(d\gamma-p)$	-7.87			0.20			0.80
15', $B(d\gamma-p)$	-7.90			0.18			0.82
25', $B(d\gamma-p)$	-8.81		0.00	0.12	0.00		0.88
25, v	-8.94					-0.04	1.04
15, v	-9.07		0.02			0.02	0.97
12', v	-9.61					-0.05	1.05
25', v	-10.70		0.00	0.00	0.02		0.97
2', v	-11.60	0.03				-0.02	0.99
1, v	-12.10	0.03		0.00	0.02		0.95

TABLE II. Atomic-orbital populations for (a) up-spin and (b) down-spin eigenfunctions of CdCr_2Se_4 at the Γ point. The figure 0.00 means less than 0.005 and the blank means exactly zero by symmetry. The abbreviated notations for the eigenfunctions, Lc and Hv , mean the lowest conduction band and the highest valence band, respectively, and other notations, $A(d\gamma-p)$ and $B(d\gamma-p)$, mean the antibonding and bonding states of the chromium $3d\gamma$ and selenium $4p$ orbitals, respectively.

Symmetry	E (eV)	Cd 5s	Cd 5p	Cr 3d	Cr 4s	Cr 4p	Se 4p
(a) up spin							
15, c	2.40		0.39			0.57	0.03
25, c	1.74					1.02	-0.02
1, c	1.32	0.54		0.00	0.33		0.14
15, c	0.19		0.17			0.83	0.00
25', c	-1.19		0.42	0.00	0.52		0.06
2', c	-2.33	0.61				0.37	0.01
1, Lc	-3.91	0.37		0.00	0.63		0.00
15', $A(d\gamma-p)$	-3.96			0.41			0.59
12, $A(d\gamma-p)$	-4.06			0.42			0.58
25', $A(d\gamma-p)$	-4.52		0.01	0.58	0.00		0.40
15, Hv	-6.26		0.00			0.04	0.96
1, $d\epsilon$	-6.66	0.00		1.00	0.00		0.00
12, $d\epsilon$	-6.68			1.00			0.00
25', $d\epsilon$	-7.01		0.00	1.00	0.00		0.00
15', $d\epsilon$	-7.03			1.00			0.00
25', $d\epsilon$	-7.08		0.00	1.00	0.00		0.00
25, v	-8.12					-0.02	1.02
15, v	-8.31		0.04			0.05	0.91
15', $B(d\gamma-p)$	-8.48			0.59			0.41
25', $B(d\gamma-p)$	-8.59		0.01	0.42	0.01		0.57
12, $B(d\gamma-p)$	-8.70			0.58			0.42
12', v	-9.39					0.03	0.97
25', v	-10.49		0.01	0.00	0.12		0.86
2', v	-11.04	0.09				0.02	0.89
1, v	-11.63	0.10		0.00	0.04		0.86
(b) down spin							
15, c	3.02		0.41			0.56	0.02
25, c	2.88					1.04	-0.04
1, c	1.61	0.46		0.00	0.44		0.10
15, c	0.67		0.25			0.75	0.00
25', c	-0.51		0.51	0.01	0.45		0.03
15', $A(d\gamma-p)$	-1.58			0.77			0.23
25', $A(d\gamma-p)$	-1.66		0.02	0.86	0.00		0.12
12, $A(d\gamma-p)$	-1.67			0.77			0.23
2', c	-2.04	0.64				0.33	0.03
12, $d\epsilon$	-3.07			1.00			0.00
1, $d\epsilon$	-3.07	0.00		0.99	0.00		0.00
1, Lc	-3.34	0.44		0.01	0.54		0.01
25', $d\epsilon$	-3.49		0.00	1.00	0.00		0.00
15', $d\epsilon$	-3.50			1.00			0.00
25', $d\epsilon$	-3.58		0.00	1.00	0.00		0.00
15, Hv	-6.39		0.00			0.02	0.98
15', $B(d\gamma-p)$	-7.38			0.23			0.77
12, $B(d\gamma-p)$	-7.59			0.23			0.77
25', $B(d\gamma-p)$	-7.95		0.01	0.13	0.00		0.85
25, v	-8.22					-0.04	1.04
15, v	-8.39		0.04			0.03	0.93
12', v	-9.41					-0.03	1.03
25', v	-10.36		0.02	0.00	0.05		0.93
2', v	-11.09	0.10				-0.02	0.92
1, v	-11.60	0.10		0.00	0.01		0.89

TABLE III. Characteristic data of the calculated band structure for CdCr_2S_4 and CdCr_2Se_4 .

		CdCr_2S_4	CdCr_2Se_4
Conduction bands			
lowest bandwidth		4.5 eV	3.9 eV
minimum point symmetry		Λ_1	Γ_1
<i>d</i> -bandwidth	<i>dε</i> †	0.5 eV	0.4 eV
	<i>dγ</i> †	1.3 eV	1.5 eV
	<i>dε</i> ‡	0.3 eV	0.1 eV
	<i>dγ</i> ‡	0.9 eV	1.0 eV
Valence bands			
total bandwidth	†	5.2 eV	5.4 eV
($\Gamma_{15,Hv} - \Gamma_{1,v}$)	‡	4.9 eV	5.2 eV
highest bandwidth		0.5 eV	0.5 eV
maximum point symmetry		Σ_4	Σ_4
Energy gap at Γ point	†	2.6 eV	2.3 eV
($\Gamma_{1,Lc} - \Gamma_{15,Hv}$)	‡	3.4 eV	3.1 eV

bottom just mentioned, in which the $4p$ of Cr is a slightly larger component for sulfide while the $5s$ of Cd is a larger component for selenide. The admixture of the $3d\gamma$ orbitals of Cr and the p orbital of anion leads to two groups of levels, $B(d\gamma-p)$ and $A(d\gamma-p)$, in Tables I and II. The lower group $B(d\gamma-p)$, corresponding to the bonding orbitals in the language of the molecular-orbital (MO) theory, lies well inside the valence bands and the upper antibonding group $A(d\gamma-p)$ falls in the lower conduction-band range. The anion p component of wave functions in the $B(d\gamma-p)$ bands which is fully occupied is about 50% for the up spin and about 80% for the down spin. This leads to a remarkable conclusion that the spin polarization on chalcogen ions is small but has the opposite sign to that on the Cr ions, that is to say, a kind of ferrimagnetic feature shows up, at least, in the viewpoint of the Mulliken population analysis (see also Table IV).

The characteristic data of the calculated band structures, e.g., the width of the bands, the max-

imum point of the valence bands, the minimum of the conduction bands, and the gap energy, are tabulated in Table III. The top of the valence bands has the Σ_4 symmetry, being at a point one-third away from Γ to K , both for sulfide and for selenide, which is slightly higher than the Γ_{15} level. The bottom of the conduction bands has the Λ_1 symmetry in sulfide and the Γ_1 in selenide.

Table IV shows self-consistent Mulliken charge population obtained for each atomic shell. The spin polarization of the $3d$ orbitals is about 3.5, of which 0.5 comes from the $3d\gamma$ component mixed in the $B(d\gamma-p)$ bands, for sulfide and selenide. This spin polarization of the Cr ion is slightly enhanced by the $4s$ and $4p$ contributions. In contrast, the spin polarization of the chalcogen ion is opposite in sign, the magnitude of which is about 0.3 for both compounds. It is also seen from Table IV that the back donation from the chalcogen p orbitals to the s and p orbitals of Cd and Cr is considerably larger for selenide. In this connection it should be noted that Se is more covalent than S.

IV. DISCUSSIONS

Some of the different features between the calculated band structures of CdCr_2S_4 and CdCr_2Se_4 are pointed out and discussed below, although their band structures are quite similar as mentioned in the last section. The band widths and gap energies of the selenide are generally smaller by 10–20% than the corresponding quantities of the sulfide but for a few exceptions. The larger lattice constant of selenide seems enough to explain this difference as discussed in I. The symmetry of the bottom of the conduction band is different between both compounds as shown in Table III; the transition corresponding to the fundamental absorption edge is strongly indirect in sulfide, whereas it is almost direct in selenide.

The spin polarization of the p orbitals of the chalcogen ion is one order of magnitude smaller

TABLE IV. Self-consistent Mulliken charge populations for each atomic shell of CdCr_2S_4 and CdCr_2Se_4 .

		CdCr_2S_4			CdCr_2Se_4		
		†	‡	total	†	‡	total
Cd	$5s$	0.07	0.07	0.22	0.16	0.16	0.58
	$5p$	0.04	0.04		0.13	0.14	
	$3d$	3.82	0.30		3.92	0.35	
Cr	$4s$	0.12	0.05	4.33	0.16	0.07	4.61
	$4p$	0.06	-0.02		0.10	0.01	
S or Se	np	2.47	2.81	5.28	2.34	2.71	5.05

than that of the $3d$ of Cr, but it has the sign opposite to the latter. If this is a real effect, its magnitude would be large enough to be detected experimentally, e.g., by a precise analysis of neutron magnetic scattering. Ohsawa *et al.*¹¹ reported that negative spin-polarization regions were observed near sulfur ions in ferromagnetic pyrite CoS_2 . Such experiments have not been done for chromium spinels yet. The $3s$ orbital of S (and $4s$ of Se) is frozen and its spin polarization is not obtained in the present calculation. If the s orbital is properly treated, its spin polarization would be much like that of p orbitals and would make a large internal magnetic field through the Fermi contact interaction. An internal magnetic field at the Se nucleus was also measured by nuclear magnetic resonance on ^{77}Se in these substances.^{12,13} The experimental findings seem to be consistent with results of the present calculation.

The band structures calculated in the present treatment DV- $X\alpha$ are compared with those of I in the semiempirical EHT. In the latter, the width of the lowest conduction band is very narrow, less than 0.8 eV, and the width of the highest valence band is 1.5 eV in sulfide and 0.9 eV in selenide. These features are reversed in the present *ab initio* calculation; the width of the lowest conduction band is much wider and amounts to about 4 eV, and the width of the highest valence band is less than 0.5 eV. Our previous EHT calculation does not appear to give the correct bandwidth since we fitted the parameters so as to reproduce the band structure of nonmagnetic spinel CdIn_2S_4 only at the Γ point. The symmetry of the bottom of the conduction bands is identical for both calculations. However, the top of the valence bands in the present calculation has the Σ_4 symmetry in disaccord with the conclusion of I and it is interesting that the previously reported band structure of CdIn_2S_4 has the same feature.^{14,15} The direct gap in the present calculation is a little larger than the EHT results and agreement with the experiments¹⁶ is quite good, although a very conclusive statement cannot be given at this point be-

cause the experimental data available for the time being have, still, a slight fluctuation. The features of the d bands are qualitatively identical, but the $d\epsilon$ and $d\gamma$ bands of up spin fall in the top region of the valence band and just below the lowest conduction band, respectively, in the present calculation, whereas the separation between the $d\epsilon$ and $d\gamma$ bands is smaller and both d bands lie completely in the fundamental gap in I. Some optical observations seem to favor this new feature of d bands.

Finally, a few general comments will be given below on the present calculation. First of all, it is emphasized that the present calculation has been carried out self-consistently. Spin-polarized self-consistent calculations have rarely been done on such a large system without any restriction on the crystal potential. This large calculation has been made feasible by using the DV- $X\alpha$ method. A self-consistent treatment is essential in order to discuss the spin polarization from the first principle. It is, of course, desired to refine the accuracy of the calculations and it is hoped that the refinement is made possible very soon. The calculations along this line are in progress and in preparation for other chromium spinels, HgCr_2Se_4 and CuCr_2X_4 ($X = \text{S}, \text{Se}$), magnetic and nonmagnetic semiconductors with chalcopyrite structure, CuFeS_2 , CuAlS_2 , and CuGaS_2 , and some pyrite compounds.

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