

Self-consistent electronic structures of magnetic semiconductors by a discrete variational $X\alpha$ calculation. II. HgCr_2Se_4

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The electronic band structure of a ferromagnetic semiconducting spinel HgCr_2Se_4 is self-consistently calculated by using the discrete variational $X\alpha$ method. The overall features of the band structure are quite similar to those of CdCr_2S_4 and CdCr_2Se_4 , which have been calculated in the first paper of this series [T. Oguchi, T. Kambara, and K.I. Gondaira, *Phys. Rev. B* **22**, 872 (1980)]. The fundamental energy gap is 1.8 eV, somewhat narrower than those of the Cd compounds. The narrowest band gap appears between the $d\epsilon$ and $d\gamma$ bands, and its width is 0.4 eV, much smaller than those of the Cd compounds. The top of the valence bands has the Σ_4 symmetry and the bottom of the conduction bands Γ_1 . The spin polarization of the $3d$ orbitals of Cr is about 3.5, of which 0.5 comes from the $3d$ components mixed in the valence bands, while the spin polarization of the $4p$ orbitals of Se has the opposite sign, the magnitude of which is about 0.3.

I. INTRODUCTION

A chromium spinel HgCr_2Se_4 is a ferromagnetic semiconductor and its optical, electrical, and magnetic properties have been continuously studied as well as the same type of magnetic semiconductors CdCr_2S_4 and CdCr_2Se_4 , the electronic structures of which we calculated and discussed in the preceding paper¹ (hereafter referred to as I). The most prominent property of HgCr_2Se_4 is that its optical absorption edge takes an anomalously low value of energy, about 0.3 eV at 4.2 K to be compared with 1.8 and 1.2 eV of CdCr_2S_4 and CdCr_2Se_4 , respectively. A very large red shift of the absorption edge with decreasing temperature has been reported to amount to 0.5 eV,² twice as large as those of the Cd compounds. There has been no definite interpretation of those noticeable properties yet.

Several authors³ have reported the results of observations for the electric conduction properties and their correlation with the magnetic properties. Among these a rapid decrease of the conductivity and a giant negative magnetoresistance near the Curie temperature are remarkable. Although the interpretations of these have been given, at least, partially, a unified and systematic understanding has not been given yet.

In order to get the reliable basis for a full understanding of these properties, we calculate the electronic band structure of HgCr_2Se_4 by use of the discrete variational (DV) $X\alpha$ method which we used in I to calculate the band structures of CdCr_2S_4 and CdCr_2Se_4 , and discuss characteristic features of the band, comparing them with those of the Cd compounds. Since the calculations are carried out self-consistently without such a serious approximation for the potential as the muffin-tin approximation, a good deal of quantitative dis-

cussions based on the calculated results are quite feasible for such a large system as spinels.

II. COMPUTATIONAL METHOD

The calculations in this paper have been performed along the same procedure as used and described in detail in I. Therefore, we give here only a brief summary of the computational procedure.

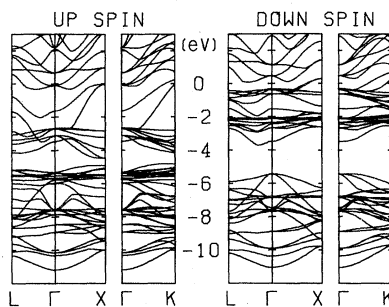
The initial crystal charge density is constructed as a superposition of atomic spherical charge densities which are generated by solving self-consistently a central-field one-electron equation for each atom. The Coulomb and exchange potentials are represented in terms of the local crystal charge density. The exchange scaling parameter α of the $X\alpha$ potential is fixed to 0.7.⁴ We use as the basis functions the numerically generated atomic orbitals: $1s \sim 6p$ for Hg and $1s \sim 4p$ for Cr and Se. The frozen core approximation⁵ is adopted and the valence-electron orbitals are orthogonalized to all core orbitals, to make the calculation tractable. The overlap and Hamiltonian matrix elements are evaluated by using the random sampling integration where a sum of Fermi-type functions around each atom is adopted as the distribution function of the sample points.⁶ We use a total of 3000 sample points in a unit cell and the error in the occupied band energies is within 0.2 eV. An iterative procedure is employed to get the solution. The self-consistent-charge method⁷ is adopted, that is, the self-consistency is attained between the input and output atomic-orbital populations. Only a few iterations are needed to obtain the populations within an error of 0.02.

III. RESULTS AND DISCUSSION

A. Band structure

The calculated band structure of HgCr_2Se_4 in the ferromagnetic phase is shown along the three symmetry lines of the Brillouin zone in Fig. 1. The general feature of the band structure is quite similar to those of CdCr_2S_4 and CdCr_2Se_4 calculated in I: The band structure consists of relatively narrow valence bands, fairly wide conduction bands, and very narrow d bands. The up- and down-spin bands look essentially the same, except that the locations of the $3d$ bands of Cr relative to the valence and conduction bands are quite different.

The energy eigenvalues and the component of the eigenfunctions at the Γ point are listed in Table I. The valence bands are composed mainly of the $4p$ orbitals of Se and their total width is 5.9 eV for the up spin and 5.6 eV for the down spin. The top of the valence bands has the Σ_4 symmetry, being at a point one-third away from Γ to K , and consists of only the $4p$ orbitals of Se. The bottom of the conduction bands has Γ_1 symmetry and is composed of the $4s$ orbitals of Cr with large mix-

FIG. 1. Band structure of HgCr_2Se_4 .

ing with $6s$ of Hg. The energy gap at the Γ point of the Brillouin zone is 1.8 eV, somewhat smaller than those of CdCr_2S_4 and CdCr_2Se_4 , which are 2.6 and 2.3 eV, respectively. The magnitude of the energy gaps for three compounds is, in fact, in the order expected because of the following facts. The position of the highest valence band relative to the Cr $3d$ bands changes mainly with the species of the anion: It is lower for sulfides than for selenides. The position of the lowest conduction band relative to the Cr $3d$ bands changes

TABLE I. Atomic orbital populations for (a) up-spin and (b) down-spin eigenfunctions of HgCr_2Se_4 at Γ point, where only one or two dominant components are listed. The abbreviated notations for the energy levels LC and HV mean the lowest conduction band and the highest valence band, respectively, and other notations, $A(dp)$ and $B(dp)$, mean the anti-bonding and bonding states of Cr $3d$ and Se $4p$ orbitals, respectively. An arrow shows the forbidden gap.

(a) up spin				(b) down spin			
Symmetry	E (eV)	Populations (%)		Symmetry	E (eV)	Populations (%)	
$15, c$	3.08	Hg $6p$ (53)	Cr $4p$ (43)	$15, c$	3.52	Hg $6p$ (51)	Cr $4p$ (46)
$25, c$	2.20	Cr $4p$ (103)		$25, c$	3.24	Cr $4p$ (104)	
$1, c$	2.09	Hg $6s$ (43)	Cr $4s$ (33)	$1, c$	2.89	Cr $4s$ (36)	Hg $6s$ (33)
$15, c$	0.66	Cr $4p$ (83)	Hg $6p$ (16)	$15, c$	1.13	Cr $4p$ (75)	Hg $6p$ (25)
$25', c$	-0.10	Hg $6p$ (54)	Cr $4s$ (37)	$25', c$	0.46	Hg $6p$ (53)	Cr $5s$ (27)
$2', c$	-1.64	Hg $6s$ (72)	Cr $4p$ (24)	$12, A(dp)$	-0.32	Cr $3d\gamma$ (74)	Se $4p$ (26)
$12, A(dp)$	-2.67	Se $4p$ (52)	Cr $3d\gamma$ (48)	$15', A(dp)$	-0.38	Cr $3d\gamma$ (76)	Se $4p$ (24)
$15', A(dp)$	-2.71	Se $4p$ (54)	Cr $3d\gamma$ (46)	$25', A(dp)$	-0.64	Cr $3d\gamma$ (75)	Hg $6p$ (12)
$25', A(dp)$	-3.11	Cr $3d\gamma$ (63)	Se $4p$ (41)	$2', c$	-1.53	Hg $6s$ (74)	Cr $4p$ (21)
$1, LC$	-3.47	Cr $4s$ (63)	Hg $6s$ (35)	$15', d\epsilon$	-2.08	Cr $3d\epsilon$ (100)	
$15, HV$	-5.32	Se $4p$ (96)		$25', d\epsilon$	-2.11	Cr $3d\epsilon$ (95)	
$25', d\epsilon$	-5.38	Cr $3d\epsilon$ (91)		$25', d\epsilon$	-2.36	Cr $3d\epsilon$ (96)	
$15', d\epsilon$	-5.54	Cr $3d\epsilon$ (100)		$1, d\epsilon$	-2.44	Cr $4s$ (54)	Cr $3d\epsilon$ (40)
$25', d\epsilon$	-5.68	Cr $3d\epsilon$ (98)		$12, d\epsilon$	-2.68	Cr $3d\epsilon$ (100)	
$1, d\epsilon$	-5.78	Cr $3d\epsilon$ (82)	Hg $6s$ (13)	$1, LC$	-3.49	Hg $6s$ (53)	Cr $3d\epsilon$ (38)
$12, d\epsilon$	-5.97	Cr $3d\epsilon$ (100)		$15, HV$	-5.43	Se $4p$ (97)	
$15, v$	-7.57	Se $4p$ (90)		$25', B(dp)$	-6.79	Se $4p$ (80)	Cr $3d\gamma$ (17)
$25', B(dp)$	-7.58	Se $4p$ (52)	Cr $3d\gamma$ (46)	$15', B(dp)$	-6.85	Se $4p$ (76)	Cr $3d\gamma$ (24)
$25, v$	-7.62	Cr $4p$ (103)		$12, B(dp)$	-7.48	Se $4p$ (74)	Cr $3d\gamma$ (26)
$15', B(dp)$	-7.86	Cr $3d\gamma$ (54)	Se $4p$ (46)	$15, v$	-7.59	Se $4p$ (93)	
$12, B(dp)$	-8.47	Cr $3d\gamma$ (52)	Se $4p$ (48)	$25, v$	-7.68	Se $4p$ (104)	
$12', v$	-8.93	Se $4p$ (98)		$12', v$	-8.90	Se $4p$ (103)	
$25', v$	-10.16	Se $4p$ (82)	Cr $4s$ (10)	$25', v$	-9.91	Se $4p$ (92)	
$2', v$	-10.33	Se $4p$ (89)	Hg $6s$ (10)	$2', v$	-10.37	Se $4p$ (92)	Hg $6s$ (10)
$1, v$	-11.20	Se $4p$ (79)	Cr $3d$ (11)	$1, v$	-11.06	Se $4p$ (85)	Hg $6s$ (10)

mainly with the species of the A-site cation: It is lower for Hg compounds than for Cd compounds.

The exchange splitting of the Cr 3d bands is very large; it amounts to 3 eV. The 3d bands of Cr for each spin split into two groups, lower $d\epsilon$ (d_{yz}, d_{zx}, d_{xy}) and higher $d\gamma$ ($d_{x^2-y^2}, d_{z^2}$) bands, as expected for an octahedrally coordinated site. The $d\epsilon$ bands are composed of almost pure 3d ϵ orbitals of Cr and lie in the energy region of, roughly, the top of the valence bands for the up-spin electrons and in the conduction bands for the down-spin electrons. The $d\gamma$ bands, $A(dp)$ in Table I, are composed of the 3d γ orbitals of Cr considerably hybridized with the 4p orbitals of Se, which are nothing but the antibonding states in the molecular-orbital theory of the covalent bonding, and they lie around the lowest conduction band for both spins. On the other hand, the bonding partner $B(dp)$ of $A(dp)$ lies in the valence bands. The narrowest band gap appears between the $d\epsilon$ and $d\gamma$ bands at the X point and its width is 0.4 eV which is much smaller than those of the Cd compounds. The characteristic data of the band structure for HgCr₂Se₄ are summarized in Table II. It is strongly suggested from the energy gap shown in Table II that the low-energy absorption edge corresponds to the transition from the highest $d\epsilon$ band to the lowest $d\gamma$ at the X point. Although $d-d$ transitions in an isolated Cr ion are expected, as usual, to have rather low intensity, it might be possible that the considerable admixture of Se 4p orbitals into the $d\gamma$ levels gives the transition a sort of charge-transfer nature and consequently makes the corresponding absorption much more intense.

TABLE II. Characteristic data of the calculated band structure for HgCr₂Se₄.

HgCr ₂ Se ₄		
Conduction bands		
lowest bandwidth		3.5 eV
minimum point		Γ_1
	$d\epsilon \uparrow$	1.2 eV
	$d\gamma \uparrow$	1.8
d -band width		
	$d\epsilon \downarrow$	0.6
	$d\gamma \downarrow$	1.5
Valence bands		
total bandwidth	\uparrow	5.9 eV
($\Gamma_{15}, HV - \Gamma_1, \nu$)	\downarrow	5.6
highest bandwidth		1.0
maximum point		Σ_4
Energy gap at Γ point	\uparrow	1.8 eV
($\Gamma_1 LC - \Gamma_{15}, HV$)	\downarrow	1.9
Minimum energy gap		0.4 eV
symmetry point		X

Another possibility for the interpretation of the low-energy absorption edge is mentioned here. It would be also possible that if the spin-orbit coupling which has been neglected in the present calculation is taken into consideration some of the energy levels split and are shifted by an order of magnitude of, typically, electron volts and the photon energy of the transition with stronger intensity expected, e.g., the transition from the top of the valence band to the $d\gamma$ state at the Γ point, becomes much lower so as to be consistent with the observed absorption edge. If both of the initial and final states are essentially of d character, the origin of the red shift is unlikely to be due to the ordinary Zeeman shift of the relevant levels; the many-electron effect, that is, the intraionic correlation energy may be important to explain the observed red shift. This problem still remains to be solved as well as the effect of the spin-orbit coupling on the band structure.

B. Charge population

The self-consistent Mulliken charge populations are shown in Table III for HgCr₂Se₄. The saturation magnetic moment turns out to be $6\mu_B$ per formula unit (two Cr atoms). The value obtained for the magnetic moment agrees very well with the susceptibility measurement by Wakaki *et al.*⁸ The spin polarization of the 3d orbitals of Cr is about 3.5, of which 3 comes from the occupied Cr 3d ϵ orbitals of up spin where the hybridization with other orbitals is negligibly small in magnitude though allowed in symmetry. The extra contribution of 0.5 to the 3d polarization comes from the 3d γ components mixed in the Se 4p-like bonding states $B(dp)$. It should be noted that the spin polarization of the 4p orbitals of Se is small but finite and opposite to that of the 3d of Cr in sign, at least, in the viewpoint of the Mulliken population analysis.

The occurrence of the negative-spin polarization of the chalcogen ion, which has been seen also for CdCr₂S₄ and CdCr₂Se₄, can be understood in the following way. The 3d γ of Cr and the 4p of Se are hybridized to yield the pair of bonding and antibonding states. The up-spin electrons of those which occupy the bonding states are attracted onto the Cr ions owing to the exchange interaction with the localized moment on the Cr ions. It is not the case for the down-spin electrons and they yield eventually the opposite-sign polarization on the Se sites. If the small negative-spin polarization of Se found in the present calculation is rather localized spatially, it could be detected by neutron diffraction study. The neutron diffraction study has not been done for HgCr₂Se₄ yet, however.

TABLE III. Self-consistent Mulliken charge populations for each atomic shell of HgCr_2Se_4 .

		HgCr_2Se_4		
	†	‡		Total
Hg	6s	0.23	0.19	0.75
	6p	0.17	0.16	
	3d	3.85	0.46	4.64
Cr	4s	0.16	0.06	
	4p	0.10	0.01	
Se	4p	2.34	2.65	4.99

It is seen that the back donation from the chalcogen p orbitals to the outermost s and p orbitals of the A-site metal ions (Hg or Cd) is the largest for HgCr_2Se_4 among the three materials CdCr_2S_4 ,

CdCr_2Se_4 , and HgCr_2Se_4 . This indicates that HgCr_2Se_4 is the most covalent of the three, and is in accord with the narrowest band gap or absorption edge.

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