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Band Structure Calculation of $\text{Mn}_x\text{Co}_y\text{Fe}_{3-x-y}\text{O}_4$

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Abstract. Electronic band structure of $\text{Mn}_x\text{Co}_y\text{Fe}_{3-x-y}\text{O}_4$ has been calculated in high symmetrical points and lines of the first Brillouin zone within the scope one-electron quasirelativistic pseudopotential approach. Atomic potential form-factors have been calculated in accordance with modified LCAO method. Dependence of energy gap $E_g = E_g(x, y)$ against Mn, Co and Fe concentrations is calculated and presented.

We assumed that the solid solution $\text{Mn}_x\text{Co}_y\text{Fe}_{3-x-y}\text{O}_4$ (MCFO) [1] is crystallized in structures with Γ_c^2 Bravais lattice and space group symmetry O_h^7 . Eight formulas units form the elementary cell. The main vectors of reciprocal lattice and high symmetrical points and lines coordinates have been extracted from [2]. Lattice parameters $a=a(x, y)$ have been measured experimentally (Table 1). The basic vectors $(\vec{r}_s)$ for

Table 1. Lattice constants for MCFO spinels

x	y	Lattice constant (nm)
0.44	0.18	0.8449
0.00	1.00	0.8395
0.12	1.00	0.8408
0.45	0.98	0.8419
0.94	1.05	0.8435
0.40	0.93	0.8415

coordinates of nonequivalent ions in elementary cell have been obtained from [3].

It is well-known that spin-orbit interaction influences on the band structure and optical characteristics such material as Ni ($Z(\text{Ni})=28$, further Z - is the total nuclear charge for one MCFO chemical formula) [4]. So the spin-orbit interaction term has been taken into account and electronic band structure of MCFO has been calculated within the scope one-electron pseudopotential approach by means of quasirelativistic Schrodinger equation solving [5]

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) + \frac{\hbar}{4m^2 c^2} \vec{\sigma} [\nabla V, \vec{p}] \right\} \Psi = E \Psi \quad (1)$$

which is equivalent to the system of equations:

$$\begin{aligned} (T+V)\Psi_1 + \frac{\hbar}{4m^2 c^2} [l_3 \Psi_1 + (l_1 - il_2) \Psi_2] &= E_1 \Psi_1, \\ (T+V)\Psi_2 + \frac{\hbar}{4m^2 c^2} [(l_1 + il_2) \Psi_1 - l_3 \Psi_2] &= E_2 \Psi_2 \end{aligned} \quad (2)$$

where $T = -\frac{\hbar^2}{2m} \nabla^2$, Ψ_r (τ - is the spin index, $\tau = 1$ for spin in "up"-state, $\tau = 2$ for spin in "down"-state) - is a spinor

component for valent electron, $l_i = \varepsilon_{ijk} \frac{\partial}{\partial x_j} p_k$, $p_k = -i\hbar \frac{\partial}{\partial x_k}$, $\vec{r} = (x_1, x_2, x_3)$.

$$\Psi_r = \Psi_{br\mu\nu}^j(\vec{r}) = \sum_{m=1}^N \alpha_{bm}^j SPW_{br\mu\nu m}^j(\vec{r}),$$

$$SPW_{br\mu\nu m}^j(\vec{r}) = \sum_{l=1}^h C_{\mu\nu}^j(l, m) \chi_{br} \exp[i\alpha_l(\vec{k} + \vec{B}_m)\vec{r}],$$

$$C_{\mu\nu}^j(l, m) = D_{\mu\nu}^{j*}(l) \exp[-i\alpha_l(\vec{k} + \vec{B}_m)\vec{r}_l],$$

$\chi_{br} - \tau$ -component of the valent electron spin function. $D_{\mu\nu}^j(l) - (\nu, \mu)$ -th matrix element of the j -th irreducible representation for α_l - l -th element of the point subgroup G_{O_k} of the wavenumber group $G_{\vec{k}} - m$ -counter of the reciprocal lattice vector $\vec{B}_m$, h - number of the elements in G_{O_k} , $\vec{r}_l$ - nontrivial translation for α_l . The electron potential energy $V(\vec{r})$ is a superposition of the such energies in a vicinity of s -th atom in p -th primitive cell ($\vec{R}_p$ - is a lattice vector):

$$V(\vec{r}) = \sum_{p,s} v^s(\vec{r} - \vec{R}_p - \vec{e}_s). \quad (3)$$

Let us transform (1,2) to a generalized eigenvalue problem $HX = ESX$, where X - the vector-function, H, S - Hermitian $N \times N$ matrices with matrix elements:

$$H_{nm} = \frac{\pi^2}{2m} (\vec{k} + \vec{B}_m)^2 \sum_{l'=1}^h C_{\mu\nu}^{l'*}(l', n) \chi_{b\tau}^* \sum_{l=1}^h C_{\mu\nu}^l(l, m) \chi_{b\tau} \delta(\vec{B}_{l'mn}) + \frac{1}{\Omega_0} \sum_{l=1}^h C_{\mu\nu}^{l'*}(l', n) \chi_{b\tau}^* \sum_{l=1}^h C_{\mu\nu}^l(l, m) \chi_{b\tau}^* \exp[i\vec{B}_{l'mn} \vec{\tau}_s] v^s(\vec{B}_{l'mn}) + \frac{\pi}{(2mc)^2} \sum_{l=1}^3 \sum_{\tau=1}^2 \sigma_{\tau}^{(l)} \epsilon_{IKL} \sum_{l'=1}^h C_{\mu\nu}^{l'*}(l', n) \chi_{b\tau}^* \sum_{l=1}^h C_{\mu\nu}^l(l, m) \chi_{b\tau} \frac{1}{\Omega_0} \sum_s \exp[i\vec{B}_{l'mn} \vec{\tau}_s] * (-i\hbar) [\alpha_i(\vec{k} + \vec{B}_m)]_{Lz} \int_{\Omega} \exp[i\vec{B}_{l'mn} \vec{r}] \frac{\partial v^s}{\partial x_K} d\vec{r}; \quad S_{nm} = \sum_{l=1}^h C_{\mu\nu}^{l'*}(l', n) \chi_{b\tau}^* \sum_{l=1}^h C_{\mu\nu}^l(l, m) \chi_{b\tau} \delta(\vec{B}_{l'mn}) \quad (4)$$

where $\vec{B}_{l'mn} = \alpha_i(\vec{k} + \vec{B}_m) - \alpha_i(\vec{k} + \vec{B}_n)$, $\delta(\vec{B}_{l'mn})$ - Kroneker's symbol, Ω_0 - the primitive cell volume, Ω - the crystal volume, $\sigma(I)$ - the I -th Pauli matrix. $v^s(\vec{B}_{l'mn})$ is the Fourier component of atomic potential v^s which has been extracted from [6]. L is the Cartesian coordinate. For cation sublattice of MCFO $v^s = (v(Mn)x + v(Co)y + v(Fe)(3-x-y))/3$. For $K=1, L=2$ integral in (4) has the form:

$$(-i\hbar) [\alpha_i(\vec{k} + \vec{B}_m)]_{Lz} \int_{\Omega} \exp[i\vec{B}_{l'mn} \vec{r}] \frac{\partial v^s}{\partial x_K} d\vec{r} = 4\pi(-i\hbar) [\alpha_i(\vec{k} + \vec{B}_m)]_{Lz} \sum_{JM} \sum_{nq} i^n \langle nqbr | JM \rangle Y_{nq}^*(\vec{r}_K)^* \sum_{q\tau} \langle nqbr' | JM \rangle \chi_{b\tau} \left[\sqrt{\frac{2\pi}{3}} (\delta_{n1}\delta_{q-1} - \delta_{n1}\delta_{q1}) \right] \sum_i \beta_i \left\{ n_i \int_0^{\infty} j_n(B_{l'mn}r) r^{n_i+1} e^{-\gamma r} dr - \gamma_i \int_0^{\infty} j_n(B_{l'mn}r) r^{n_i+2} e^{-\gamma r} dr \right\}$$

where $\int_0^{\infty} j_n(kr) r^{m+1} e^{-\gamma r} dr = \frac{k^{n+1/2} \Gamma(m+n+2)}{2^{n+1/2} (\gamma^2 + k^2)^{(n+m+2)/2} \Gamma(n+3/2)} F\left(\frac{n+m+2}{2}, \frac{n-m}{2}, n+3/2, \frac{k^2}{\gamma^2 + k^2}\right)$

$\langle nqbr | JM \rangle$ - Clebsch-Gordon coefficient [7], $F(a, b, c, z)$ - hypergeometrical function.

Band structure calculations have been carried out in points Γ, X' and along lines Δ', Σ for x, y from Table 1. The results of band gap (E_g) calculation for MCFO is presented in Fig. 1. If Z - is the total nuclear charge for one MCFO chemical formula then we can to take into account that (E_g) is increased when Z is decreased. The results of band structure calculation are presented and discussed.

Fig. 1. Band gap of MCFO spinels

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