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BANDS AND BONDS OF INTERCALATION COMPOUNDS OF LAYERED TRANSITION-METAL DICHALCOGENIDES

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Abstract. - Electronic band structures of non-magnetic and ferromagnetic states of Fe$_2$TiS$_2$ are calculated on the basis of a self-consistent APW method. Bond orders have been calculated also to get an insight into bonding nature of the intercalant atoms. The results of calculation show that d orbitals of intercalant atoms hybridize strongly with S-p orbitals.

Intercalation of 3d transition-metals into layered transition-metal dichalcogenides causes quite dramatic changes in physical properties of the host materials. To understand electronic and magnetic properties of intercalation compounds $M_2$TiS$_2$ ($M =$ transition-metal) we have made a self-consistent APW band calculation for non-magnetic states of FeTiS$_2$, CrTiS$_2$, Fe$_{1/3}$TiS$_2$ and Co$_{1/3}$TiS$_2$, and for ferromagnetic states of Fe$_{1/3}$TiS$_2$ and FeTiS$_2$ [1, 2]. The density of states (DOS) and the partial DOS obtained by us show that the band structures near the Fermi level of the mother crystal $1T$ - TiS$_2$ are modified significantly and that the M-3d states strongly hybridize with the S-3p and Ti-3d states. These theoretical results are supported by various kinds of experimental measurements [3-6].

Analysis of partial DOS tells us the extent of mixing of t-components within the muffin-tin (MT) spheres, but it cannot inform us of the nature of bonding between atoms. The purpose of the present paper is to calculate the bond orders [7] of TiS$_2$ and FeTiS$_2$ in order to clarify the bonding nature.

The crystal structure of $1T$ - TiS$_2$ consists of a sequence of S-Ti-S sandwiches. Each Ti ion is surrounded almost octahedrally by six sulphur ions. In FeTiS$_2$ iron atoms occupy all the available octahedral sites between the neighboring sulphur layers.

In figures 1a and 1b we show the DOS of TiS$_2$ and of FeTiS$_2$ obtained by us [1]. The DOS of TiS$_2$ consists of three parts, (i), (ii) and (iii) in order of increasing energy. Upon intercalation of Fe ions the original band structures of TiS$_2$ are modified strongly. The DOS of FeTiS$_2$ can be decomposed into four parts, (1), (2), (3) and (4) in order of increasing energy as shown in figure 1b.

In the APW band calculation an eigenfunction is expressed as

$$\Psi_{\mathbf{n},\mathbf{k}}(\mathbf{r}) = \sum_i c_i(\mathbf{n},\mathbf{k}) \chi_i(\mathbf{k}_i,\mathbf{r}),$$

where $n$ and $k$ are band suffix and wave vector, respectively, $\mathbf{k}_i = \mathbf{k} + \mathbf{G}_i$ with $\mathbf{G}_i$ being the $i$-th reciprocal lattice vector and $\chi_i(\mathbf{k}_i,\mathbf{r})$ denotes an augmented-plane-wave. Inside MT spheres $\chi_i(\mathbf{k}_i,\mathbf{r})$ is expressed in terms of atomic-like wave-functions and hence $\Psi_{\mathbf{n},\mathbf{k}}$ can be expressed in the $\nu$th-functions as follows:

$$\Psi_{\mathbf{n},\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{t}_m} \left[ \sum_i c_i(\mathbf{n},\mathbf{k}) A_{\mathbf{t}_m}(\mathbf{k}_i) \right] \phi_{\mathbf{t}_m}$$

where $\phi_{\mathbf{t}_m}$ represents an atomic-like wave-function centered on the $\nu$th MT sphere and $A_{\mathbf{t}_m}(\mathbf{k}_i)$ are determined by a condition that the augmented-plane-wave is continuous on the surface of the MT sphere.

Now, according to Godby et al. [7] the bond order between $\phi_{\mathbf{t}_m}$ and $\phi_{\mathbf{t}'_{m'}} (\nu \neq \nu')$ for a state $\Psi_{\mathbf{n},\mathbf{k}}$ is defined as follows:

$$\mu_{\mathbf{t}_m,\nu' \mathbf{t}'_{m'}}(\mathbf{n},\mathbf{k}) = \left< \phi_{\mathbf{t}_m} | \Psi_{\mathbf{n},\mathbf{k}} \right> \left< \Psi_{\mathbf{n},\mathbf{k}} | \phi_{\mathbf{t}'_{m'}} \right> = \left[ \sum_i C_i(\mathbf{n},\mathbf{k}) A_{\mathbf{t}_m}(\mathbf{k}_i) \right] \left[ \sum_i C_i(\mathbf{n},\mathbf{k}) A_{\mathbf{t}'_{m'}}(\mathbf{k}_i) \right].$$
We may redefine the bond order as follows:

\[
\beta_{\nu \tau m, \nu' \tau' m'}(nk) = \frac{1}{2} [\mu_{\nu \tau m, \nu' \tau m'}(nk) + \mu_{\nu \tau m, \nu' \tau m'}(n-k)].
\]  

(4)

Then, \(\beta_{\nu \tau m, \nu' \tau m'}(nk)\) is a real quantity because \(\Psi_{n-k}^* = \Psi_n^*\) and the bonding and antibonding nature is related to the sign of \(\beta_{\nu \tau m, \nu' \tau m'}(nk)\).

Calculations of the bond order of TiS\(_2\) and FeTiS\(_2\) have been made for wave vectors along the \(\Gamma M\) line.

**Bond order in TiS\(_2\).** – First we have calculated the bond order \(\beta_{Ti d\gamma, Sp}\) between the \(d\gamma\) orbital of Ti(0, 0, 0) and the p orbital of S(2/3, 1/3, 1/2). In figure 2a we plot the mean value of \(\beta_{Ti d\gamma, Sp}\) averaged over the bands in each energy range in figure 1a. The value of \(\beta_{Ti d\gamma, Sp}\) is positive and large in part (i), negative and large in part (ii), and very small in part (iii). We have also calculated the bond order between the \(d\gamma\) orbitals of the Ti ion and the p orbitals of the S ion. As the results the magnitude of \(\beta_{Ti d\gamma, Sp}\) is very small for the whole energy range.

**Bond orders in FeTiS\(_2\).** – (a) \(\beta_{Fe d\gamma, Sp}\) between the \(d\gamma\) orbital of Ti(0, 0, 0) and the p orbital of S(2/3, 1/3, 1/4): this is positive and large in part (1) and negative and large in part (4). It is small in parts (2) and (3). The magnitude of \(\beta_{Fe d\gamma, Sp}\) in FeTiS\(_2\) is reduced compared with that in TiS\(_2\). (b) \(\beta_{Fe d\gamma, Sp}\) between the \(d\gamma\) orbital of Fe(0, 0, 1/2) and the p orbital of S(2/3, 1/3, 1/4): in figure 2b the mean value of \(\beta_{Fe d\gamma, Sp}\) averaged over the bands in each energy range in figure 1b is plotted. The value of \(\beta_{Fe d\gamma, Sp}\) is positive and large in part (1) and negative and large in parts (3) and (4) while its magnitude is rather small in part (2). (c) \(\beta_{Fe d\gamma, Sp}\) between the \(d\gamma\) of Ti(0, 0, 0) and the dc orbital of Fe(0, 0, 1/2): in parts (1) and (4) its magnitude is averagely small. It is positive in part (2) and it is negative in part (3).

The above results indicate that on intercalation of Fe ions the covalent-like bond between the Ti-\(d\gamma\) and S-p states is weakened while the Fe-\(d\gamma\) states make also covalent-like bonds with the S-p states. Each part of the density of states in figure 1b can be interpreted as follows. Part (1) corresponds to the bonding bands of Ti-\(d\gamma\) and S-p mixing and of Fe-\(d\gamma\) and S-p mixing. Part (4) corresponds to the antibonding bands of Ti-\(d\gamma\) and S-p mixing while part (3) consists mainly of the antibonding states between Fe-\(d\gamma\) and S-p. As for the dc states of the Ti and Fe ions they hybridise each other and form bonding and antibonding states. Its bonding part makes a contribution to part (2) and its antibonding part constitutes part (3) together with the antibonding states between Fe-\(d\gamma\) and S-p.

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