Probabilities of Diagonal and Non-Diagonal Couplings between $d$ Electrons in Transition Metal

II. The $d$-Band-Center-Shift Energy

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Abstract

It is shown that the full account of the non-diagonal couplings between $d$ electrons sited on different atoms in a transition metal implemented in the framework of the Wills-Harrison model leads not only to vanishing the $d$-band term in the internal energy but to vanishing the whole $d$-electron-depended part of the internal energy.

Keywords: Transition metal, Wills-Harrison model, $d$-state coupling

The $d$-band energy considered in the previous paper (henceforth referred to as I) is not the single contribution due to $d$ electrons to the transition-metal internal energy in the Wills-Harrison (WH) model [1]. The second $d$-electron-depended WH energy contribution is the energy arisen because of the shift in the center of gravity of the $d$ band due to nonorthogonality of $d$-like states, $E_c$ (hereafter, per atom in atomic units):

$$E_c = \frac{z_d}{2N} \sum_{m=1}^{N} \sum_{f=1}^{N} V_c(r_{mf}),$$  \hspace{1cm} (1)

where $z_d$ is the effective $d$-electron valence, $N$ - number of atoms,

$$V_c(r) = \frac{r_d^6}{r^8} K_c,$$  \hspace{1cm} (2)
where \( r_d \) is the \( d \)-state radius, \( K_c \) - combinatoric coefficient, which as well as the coefficient \( K_b \) (paper I) in the WH approximation depends on diagonal only couplings between \( d \) electrons sited on different atoms:

\[
K_{c,WH}^{WH} = -2 \sum_{m=2}^{3} \frac{y_m x_m}{5},
\]

(3)

where \( m \) is the magnet quantum number, \( y_m = y_{|m|} \),

\[
y_0 = -45/\pi, \quad y_1 = 30/\pi, \quad y_2 = -15/2\pi,
\]

(4)

\[
x_m = x_{|m|} = \frac{1}{8} \left( 1 + \frac{4m^2 - 1}{9} \right) y_m,
\]

(5)

From (3)-(5)

\[
K_{c,WH}^{WH} = 225/\pi^2.
\]

(6)

Taking into account the probability \( p \) that all 25 \( d-d \) couplings between two different atoms in metal are equiprobable, the coefficient \( K_c \) is expressed as follows [2]:

\[
K_c = -\frac{2}{5} \left[ y_0 x_0 + \left( 2 - \frac{6p}{5} \right) (y_1 x_1 + y_2 x_2) + \right.
\]

\[
+ \frac{2p}{5} (y_0 (x_1 + x_2) + x_0 (y_1 + y_2)) + \frac{4p}{5} (y_1 x_2 + y_2 x_1) \right].
\]

(7)

If now to apply (4) and (5) to (7), the result will be similar to one obtained in the paper I:

\[
K_c = K_{c,WH}^{WH} (1-p).
\]

(8)

It denotes that at \( p = 1 \) not only the \( d \)-band energy, \( E_b \), is equal to zero, but also \( E_c \) and, consequently, the whole \( d \)-electron-depended part of the internal energy in the WH model, which is equal to \( E_b + E_c \).

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References


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