

3d-electrons contribution to cohesive energy of 3d-metals

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In this paper a model for 3d-subsystem of transition 3d-metals has been proposed and used for calculation of the cohesive energy dependent on 3d-band filling of particular metal, its bandwidth and effective intra-atomic interaction value. It has been shown that the model enables one to explain the observed peculiarities of cohesive energy effect on the atomic number. The nature of two parabolic dependencies of cohesive energy on 3d-band filling has been clarified. The calculated values of cohesive energy are close to those experimentally obtained for Sc-Ti-V-Cr-Mn-Fe series.

Key words: cohesive energy, 3d-metals, electron correlations, energy spectrum, orbital degeneracy

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1. Introduction

In figure 1, the experimental findings are presented for cohesive energy of 3d-metals depending on the atomic number (see [1], figure 3.8). Similar dependence on the atomic number is observed for melting temperatures and boiling points of 3d-metals [1, 2]. According to Friedel's theory, the cohesion energy of d-metals is defined as a sum of energies for the occupied single-electron states of a valence band [3]. If the simplest rectangular density of states is used and equivalence of d-bands is assumed, then a parabolic dependence of the cohesive energy on the number of d-electrons follows. The parabolic dependence of cohesive energy on the atomic number is in satisfactory agreement with the experimentally found dependencies for transition 4d- and 5d-metals. However, for 3d-metals, as one can see from figure 1, there are substantial qualitative discrepancies between the experimental and theoretical

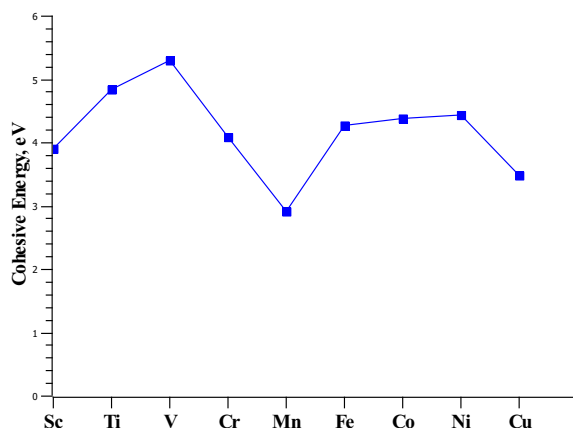


Figure 1. (Colour online) Dependence of cohesion energy on the atomic number for transition 3d-metals.

results. Clarification is necessary regarding this “two-hump” dependence and the anomaly associated with Mn. It has been shown in papers [4–6] that in non-degenerate (Hubbard) model, the cohesive energy

$$E_{\text{coh}} = \frac{n}{2}(2 - n)w - \nu U,$$

where w is the half-width of s -band, U represents the magnitude of intra-atomic Coulomb repulsion of two electrons with opposite spins on the same lattice site, n stands for the electron concentration, ν is either the doubly occupied (with two electrons on the same site) states concentration for $n < 1$ or empty sites (holes) concentration for $n > 1$. As a consequence, with interaction taken into account in the Hartree-Fock approximation, two symmetrical parabolic dependencies $E_{\text{coh}}(n)$ (for $n < 1$ and $n > 1$) as well as the peculiarity for Mn are explained.

An explanation of $E_{\text{coh}}(n)$ dependence asymmetry within the s -band model was proposed in papers [7, 8] by taking into account the electron transfer caused by electron-electron interaction, namely the correlated hopping of electrons. This way we obtain two asymmetric parabolic dependencies for $E_{\text{coh}}(n)$ with respect to $n = 1$. It is worth noting that the role of correlated hopping has been recently studied in papers [9–11] within the context of electron interactions in strongly correlated electron systems.

In the present work, developing the models [1–12], the observed peculiarities of cohesive energy effect on the atomic number in $3d$ -metals are interpreted within the framework of the model with five-fold orbital degeneracy of the band with taking into account the dependence of intraatomic interactions and $3d$ -band widths in $3d$ -metals on their filling.

2. The model

1. We represent the Hamiltonian of the model generalized for five-fold orbitally degeneracy (generalized Hubbard model) in the following form

$$H = \sum'_{ijm\sigma} t_{im,jm}(n) a_{im\sigma}^\dagger a_{jm\sigma} + H_{\text{int}}. \quad (1)$$

Here, the first term describes the delocalization energy of $3d$ -electrons, which provides the metallic bonding of atoms in crystals, $t_{im,jm}$ is the delocalization integral of electrons, $a_{im\sigma}^\dagger$, $a_{jm\sigma}$ are the operators of creation and annihilation of electrons on the lattice site in state m ($m = 1, 2, 3, 4, 5$) with spin σ ($\sigma = \uparrow, \downarrow$). In the considered model, the transfer integral $t_{im,jm}(n)$ depends on the $3d$ -electrons concentration n_d in transition $3d$ -metal. This important peculiarity of the model allows us to calculate the $3d$ -electrons contribution in the cohesive energy of particular $3d$ -metals. This is the distinction of the present model from the one proposed in paper [12] where the energy band width was assumed independent of the band filling and from “non-Hubbard-type” approach in papers [13–15].

H_{int} describes the intra-atomic interactions in the considered model and is a generalization of the Coulomb interaction term

$$U \sum_i n_{i\uparrow} n_{i\downarrow} \quad (2)$$

of the orbitally non-degenerate Hubbard model.

Let us assume that

$$H_{\text{int}} = H_1 + H_2 + H_3, \quad (3)$$

where

$$H_1 = U \sum_{im} n_{im\uparrow} n_{im\downarrow}, \quad (4)$$

$$H_2 = U' \sum_{\substack{imm_1\sigma, \\ m \neq m_1}} n_{im\sigma} n_{im_1\bar{\sigma}}, \quad (5)$$

$$H_3 = U'' \sum_{\substack{imm_1\sigma, \\ m \neq m_1}} n_{im\sigma} n_{im_1\sigma}. \quad (6)$$

Here, $n_{im\sigma}$ is an operator of electron number in the state m with spin σ on site i . The expression (4) describes the Coulomb repulsion of two electrons with opposite spins in the same orbital m , the expression (5) represents the Coulomb interaction of electrons in different orbital states ($\bar{\sigma}$ denotes the spin projection opposite to σ). The expression (6) describes the Coulomb interaction of electrons on different orbitals with taking into account the intra-atomic exchange interaction, $U > U' > U''$ (for example, see [16]).

2. The energy spectrum of electrons, with H_{int} taken into account in the Hartree-Fock approximation in the absence of magnetic ordering, is given by the expression

$$E_m(\mathbf{k}) = -\mu + t_m(\mathbf{k}), \quad (7)$$

where $t_m(\mathbf{k})$ is a Fourier component of the transfer integral $t_{im,jm}$. The chemical potential μ is renormalized by taking into account the Coulomb and exchange interactions in the Hartree-Fock approximation and is to be found from the equation for d -electron concentration

$$n_d = \int_{-w}^{\mu} \rho(\epsilon) d\epsilon, \quad (8)$$

where $\rho(\epsilon)$ is the electron density of states with taking into account the orbital degeneracy.

3. In the orbitally non-degenerate model, the cohesive energy is defined by the following expression

$$E_{\text{coh}} = -\frac{1}{N} \sum_{ij\sigma} t(n) \langle a_{i\sigma}^\dagger a_{j\sigma} \rangle - \nu U, \quad (9)$$

where the first term is the electron delocalization energy and the second one takes into account the delocalization energy lowering by polar states. In the Hartree-Fock approximation, we have

$$\nu = \frac{n^2}{4} \quad \text{for } n > 1, \quad (10)$$

$$\nu = 1 - n + \frac{n^2}{4} \quad \text{for } n < 1. \quad (11)$$

Using the model unperturbed rectangular density of electron states, we obtain

$$E_{\text{coh}} = \frac{1}{2w(n)} (w^2 - \mu^2) - \nu U, \quad (12)$$

where

$$\mu = w(n)(n - 1). \quad (13)$$

In the framework of orbitally non-degenerate model, the formula (12) reflects characteristic features of the experimentally found dependency of cohesion energy on the atomic number in 3d-metals (1).

4. Let us extend the above considerations onto the model with orbital five-fold degeneracy. We define the cohesive energy as

$$E_{\text{coh}} = \int_{-w}^{\mu} \epsilon \rho(\epsilon) d\epsilon - \nu U_{\text{eff}}(n_d), \quad (14)$$

where $U_{\text{eff}}(n_d)$ is an effective intra-atomic interaction which includes both Coulomb and intra-atomic (Hund's rule) exchange terms, ν generalizes the expressions (10), (11) of the non-degenerate model.

Following Friedel, we take

$$\rho(\epsilon) = \frac{5}{w(n_d)}, \quad (15)$$

where $w(n_d)$ is 3d-band half-width which is dependent on the band filling. Then,

$$\mu = \frac{w(n_d)n_d}{5} - w(n_d), \quad (16)$$

thus,

$$E_{\text{coh}} = 10w(n_d) \left[\frac{n_d}{10} - \left(\frac{n_d}{10} \right)^2 \right] - \nu U_{\text{eff}}(n_d). \quad (17)$$

When correlation effects can be neglected, then the cohesive energy maximum corresponds to the band center, as was obtained in the Friedel's theory [3].

3. Application for 3d-metals

1. Let us interpret a general character of the E_{coh} dependency by formula (17) on the energy parameters and the band filling in 3d-metals in terms of configurational (atom-band) model of transition metal [17, 18]. Accordingly, in the first approximation by n_d we mean the atomic values of the corresponding element, then moving on to estimations for transition metals, this statement will be corrected by taking into account s - d -transitions, which cause deviations of 3d-band filling from atomic values of n_d .

Given the peculiarities of intra-atomic interactions, represented by the expressions (4)–(6), for the case of $n_d < 5$, the Hund's polar states $3d^{n+1}$ will be relevant, for the case of $n_d > 5$, the non-Hund polar states (atomic configurations of electrons with opposite spins on different orbitals) play the role. The case of $n_d = 5$ should be considered separately, because in this case, the intra-atomic Coulomb interaction is present at the same orbital, which is considerably greater than interactions at different orbitals. For these distinct regions of n_d , the characteristic effective magnitudes of intra-atomic interactions and averaged values of bandwidth will be selected.

Let us take for all $n_d < 5$ the same values of $w(n_d)$ and $U_{\text{eff}}(n_d)$ (w_1 and U_1 , respectively). Besides, generalizing the expression (10) for non-degenerate model, we obtain

$$\nu_1 U_{\text{eff}} = 5 \left(\frac{n_d}{10} \right)^2 U_1. \quad (18)$$

Here, the intra-atomic interaction is taken into account in the Hartree-Fock approximation, ν_1 is the polar $3d^{n+1}$ -states concentration. Therefore, for $n_d < 5$

$$\frac{E_{\text{coh}}}{10w_1} = \left[\frac{n_d}{10} - \left(\frac{n_d}{10} \right)^2 \right] - \left(\frac{n_d}{10} \right)^2 \frac{U_1}{2w_1}. \quad (19)$$

In the case of $n_d > 5$, we put values w_2 and U_2 of formula (17) in correspondence with quantities $w(n_d)$ and $U_{\text{eff}}(n_d)$, and for formula (11), the corresponding expression is

$$\nu_2 U_{\text{eff}} = \left[5 - n_d + 5 \left(\frac{n_d}{10} \right)^2 \right] U_2. \quad (20)$$

In accordance with electron-hole symmetry, here ν_2 is the "hole" $3d^{n-1}$ -states concentration. For the cohesive energy in this case we obtain

$$\frac{E_{\text{coh}}}{10w_2} = \frac{n_d}{10} \left(1 + \frac{U_2}{w_2} \right) - \left(\frac{n_d}{10} \right)^2 \left(1 + \frac{U_2}{10w_2} \right) - \frac{U_2}{2w_2}. \quad (21)$$

From formulae (19) and (21) we have that $E_{\text{coh}}(n_d)$ reaches its maximum values at

$$n_d = \frac{10w_1}{2w_1 + U_1} \quad (22)$$

in the case of $n_d < 5$ and for the case of $n_d > 5$, the corresponding value is

$$n_d = \frac{10(w_2 + U_2)}{2w_2 + U_2}. \quad (23)$$

One can see that taking into account the intra-atomic interaction shifts the maximum of $E_{\text{coh}}(n_d)$ to the left or to the right from the band center.

The reasonable estimate of the intra-atomic interaction magnitude is the halfbandwidth [19]. So, we take $U_1 = w_1$ in formula (22), which leads to $n_d \approx 3$. This corresponds to the atomic value $n_d = 3$ for vanadium. In analogous way one can interpret the existence of the maximum value of E_{coh} by formula (23) for $n_d \approx 7$ (atomic value of n_d for cobalt). Hence, by formulae (19) and (21), two parabolic dependencies can be obtained with maxima specified by formulae (22) and (23). This can be put in correspondence with the experimentally found dependence of cohesive energy on atomic number, shown in figure 1.

2. For an estimation of the cohesive energy magnitudes for particular 3d-metals, we use the values for 3d-band widths and 3d-band fillings given in [1] (table 2.1), where W is the bandwidth given by [20] (table 20.4) and W^{exp} are experimental findings [21].

One can see that there is a satisfactory agreement between experimental values [20] and calculated values [1, 2] of the band widths for metals of Sc-Ti-V-Cr series.

In table 1, the results of cohesion energy calculation by formula (17) with data from table 2 are summarized. Here, E_1 are cohesion energies for the atomic values n_d (s - d -transitions neglected) and W^{exp} used. E_2 is cohesive energy from data for n_d and W^{exp} of table 2, E_3 are values of cohesive energy from data for n_d and W of table 2. E^{exp} are the experimentally found values for cohesive energy. In these calculations, an effective intra-atomic interaction has been taken equal to half-width of conduction band [19].

Note that for Sc, Ti, V, Cr, the values of W and W^{exp} are close and reliable, while for Mn, Fe, Co, Ni, these values are contradictory. For this reason, in table 2 the values for E_1 and E_2 for metals of the second group are omitted. The calculated values are close to those experimentally obtained for Sc-Ti-V-Cr-Mn-Fe sequence. Values E_3 for Co and Ni are substantially lower than the experimental findings E_{coh} (not listed in table 1), this can signal of either the inadequacy of the data listed in table 2 or the necessity to go beyond the framework used for obtaining the expressions (19) and (21), in particular, taking into account the inter-orbital transitions of electrons and go beyond the Hartree-Fock approximation. In figure 2, the values of the cohesive energy are marked red. For 3d-electrons in metals, positioned to the right of Mn, the description in terms of "configurational" (atomic) model is more appropriate, as noted in chapter 3.5 of monograph [22]. Summarizing, one can state that the proposed model not only elucidates the nature of the two-hump dependence of cohesive energy on the atomic number which is observed in transition 3d-metals and the peculiarity of E_{coh} for Mn but also leads to the values of cohesive energy close to those experimentally found for metals of Sc-Ti-V-Cr-Mn-Fe series.

Table 1. The obtained results for cohesion energy. E_1 are cohesion energies for atomic values n_d and W^{exp} used. For E_2 data for n_d and W^{exp} of table 2 were used, for E_3 data for n_d and W of table 2 were used. E^{exp} are experimental data [1, 2].

Metal	E_1 , eV	E_2 , eV	E_3 , eV	E_{coh} , eV
Sc	2.9	4.0	3.3	3.9
Ti	4.6	5.4	5.0	4.85
V	5.6	5.4	5.4	5.31
Cr	4.1	4.1	4.1	4.10
Mn			2.6	2.92
Fe			4.0	4.28

Table 2. Values for 3d-band fillings given in [1, 2], 3d-band widths W given by [20] and experimental findings W^{exp} by [21].

Metal	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
n_d	1.76	2.90	3.98	4.96	5.98	6.94	7.86	8.97
W ($2w$), eV	5.13	6.08	6.77	6.56	5.60	4.82	4.35	3.78
W^{exp} , eV	6.2	6.6	6.8	6.5	8.5	8.5	6.9	5.4

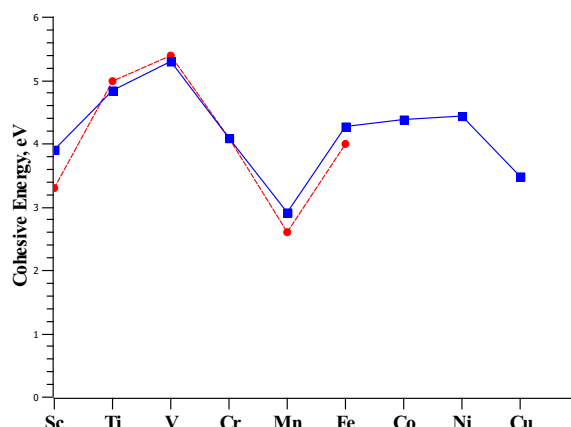


Figure 2. (Colour online) Values of cohesion energy E_3 are marked red, experimental findings are marked blue.

3. The results obtained from the calculation of $E_{\text{coh}}(n_d)$ allow one to interpret the dependencies of melting temperatures T_m for $3d$ -metals on the atomic number (analogous to the ones shown in figure 1), as the melting temperature

$$T_m = \frac{0.04E_{\text{coh}}}{k_B}, \quad (24)$$

where k_B is Boltzmann constant [1, 2].

4. Conclusions

In this paper, a model for $3d$ -subsystem of transition $3d$ -metals has been proposed and used for calculation of the cohesive energy dependent on $3d$ -band filling of a particular metal, its bandwidth and the effective intra-atomic interaction value.

It has been shown that the model allows one to explain the observed peculiarities of cohesive energy on atomic number. The nature of two asymmetric “parabolic” dependencies of cohesive energy on $3d$ -band filling has been clarified. The calculated values of cohesive energy are close to the experimentally obtained for Sc-Ti-V-Cr-Mn-Fe series. The obtained results can be extended for explaining the peculiarities of melting temperatures of transition $3d$ -metals on their atomic number and other systems [23–26] for which strong Coulomb correlations determine the peculiarities of the energy spectrum.

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Внесок 3d-електронів у енергію зв'язку 3d-металів

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В роботі запропоновано модель підсистеми 3d-електронів перехідних металів та застосовано її для розрахунку енергії зв'язку, залежної від заповнення 3d-зони конкретного металу, ширини цієї зони та величини ефективної внутрішньоатомної взаємодії. Показано, що модель дозволяє пояснити спостережувані особливості залежності енергії зв'язку від атомного номера. Пояснено природу двох параболічних залежностей енергії зв'язку від заповнення 3d-зони. Обчислені значення енергії зв'язку є близькими до отриманих експериментально для ряду Sc-Ti-V-Cr-Mn-Fe.

Ключові слова: енергія зв'язку, 3d-метали, міжелектронні взаємодії, енергетичний спектр, орбітальне виродження
