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INTERPRETATION OF DEPENDENCE BETWEEN COHESION ENERGY AND MELTING TEMPERATURE FOR TRANSITIVE 3D-METALS ON ATOMIC NUMBER

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Summary. *A model for the description of the dependence of cohesive energy and thermodynamic characteristic 3d-metals on atomic number was proposed. Obtained results explain the experimental dependences of cohesive energy and melting temperature on atomic number: «anomaly» for Mn and a presence of two non-equivalent «parabolic dependences».*

Key words: *transitive 3d-metals, melting temperature, melting point, cohesive energy, atomic number, orbital band energy, rectangular density of states, interatomic interaction, node.*

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Introduction. Transitive metals within iron group (*3d*-metals) and their compounds are of special attention due to their unique electric, magnetic, thermodynamic and mechanic properties. It is, first of all, explained with the fact that 3d-electrons manifest themselves as collectivized and quasi-localized (close to "their" ions). Associated theories facilitated remarkable success in determination of a wide range of properties being intrinsic to electric and magnetic properties of 3d-metals and their compounds. However, a number of questions associated with 3d-metals' physics, that are important both theoretically and practically, are yet not clarified. Thus, the origin of cohesion energy in 3d-metals as well as their thermodynamic characteristics (like, for example, dependencies of melting temperature, boiling temperature and elasticity modules on atomic number) are to be thoroughly studied.

Figure 1 displays the experimental values of *3d*-metals melting temperature depending on their atomic number [1].

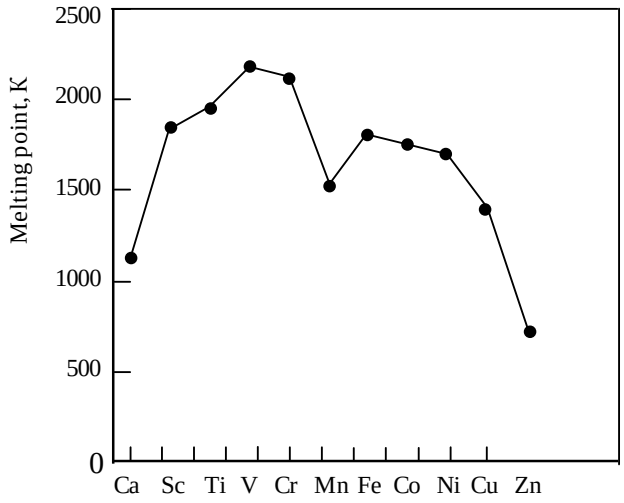

Figure 1. Melting points of the 3*d*-metals

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Similar dependency on atomic number is also spotted for *3d*-metals boiling temperature [1]. There emerges the task to find out the origin of such ("double-hump") dependency and anomaly associated with Mn.

The presented here dependency of melting temperature upon atomic number needs to be interpreted on the basis of analysis of cohesion energy as the thermodynamic characteristics are "derivative" from the latter; there exists the empiric formula linking E_{coh} in 3*d*-metals with melting temperature T_m.

A number of issues were dedicated to description of impact of band filling rate upon the changes in cohesion energy [1-5]. There was shown the important role of internal atomic interactions at cohesion energy behavior during concentration of electrons in the area. However, these issues studied the phenomena within orbital non-extinct band; it does not facilitate making adequate quantitative evaluations of *3d*-metals and their alloys cohesion energy and melting temperature.

In this research project the surveyed peculiarities of dependency between cohesion energy, melting temperature and atomic number in *3d*-metals is interpreted within a model with quintuple orbital degenerate of *3d*-band.

Model. Hamiltonian of orbital non-extinct model, which was investigated in [6] and generalized in case of quintuple orbital degenerate (Hubbard general model), is represented as

$$H = \sum_{ijm\sigma}{}' t_{im,jm} a^{+}_{im\sigma} a_{jm\sigma} + H_{int}. \qquad (1)$$

The first item here describes delocalization energy of *3d*-electrons (secures the metallic linkage of atoms inside the crystal),), $t_{im,jm}$ are "delocalization integrals" of electrons, $a^{+}_{im\sigma}$, $a_{jm\sigma}$ are operators of creation and destruction of electrons on site *i* and in orbital *m* (*m*=1, 2, 3, 4, 5) with spin σ ($\sigma = \uparrow, \downarrow$). The represented model assumes that transposition integral $t_{im,jm}(n)$ depends against Friedel model on the concentration of $3d^n$-electrons (n_d-electrons) inside the given metal.

H_{int} describes the internal atomic interactions in the investigated model and is the summary of Coulomb interaction

$$U\sum_{i} n_{i\uparrow} n_{i\downarrow} \qquad (2)$$

in orbital non-degenerate Hubbard model

This model can be briefed to

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

where

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

$$H_2 = U - J\sum_{imm_1\sigma} n_{im\sigma} n_{im_1\bar{\sigma}}, \qquad (5)$$

$$H_3 = (U - 2J)\sum_{imm_1\sigma} n_{im\sigma} n_{im_1\sigma} \qquad (6)$$

(look at [6]. Here $n_{im\sigma}$ is an operator of electrons number in condition *m* with spin σ at nodei *i*. Expression (4) describes Coulomb repulsion of two electrons with opposite spins in the same orbital condition *m*, formula (5) depicts Coulomb interaction between the electrons in different orbital conditions ($\bar{\sigma}$ indicates the spin opposite to spin σ). (6) describes Coulomb interaction between the electrons in different orbits with an eye on internal atomic exchange interaction (Hund interaction *J*).

Cohesion energy. In orbital non-degenerate model the cohesion energy [6]

$$E_{coh} = -\sum_{ij\sigma} t(n)\left\langle \alpha_{i\sigma}^{+}\alpha_{j\sigma}\right\rangle - \nu U\,, \tag{7}$$

where first item is an energy of electrons delocalization, and the second one considers the deduction of delocalization energy by "polar conditions".

The formula (7) assumes that hopping integral $t(n)$ depends on the rate of band filling at the expense of concentration-tied transposition integral stipulated by electron-electronic correlations (model of narrow-band material with electron-hole asymmetry [4]), $t(n)\left\langle \alpha_{i\sigma}^{+}\alpha_{j\sigma}\right\rangle$ is an average energy of electron transition with spin σ between the nearest neighbors; $\nu=d$ is a concentration of pairs, if $n<1$ and $\nu=c$ is a concentration of holes, if $n>1$ (n is an average number of electrons per a node in *s*-band).

In applied here Hartree-Fock approximation

$$\nu = \frac{n^2}{4} \quad \text{для} \quad n<1\,, \tag{8}$$

$$\nu = 1-n+\frac{n^2}{4} \quad \text{для} \quad n>1\,. \tag{9}$$

Having used the unperturbed rectangular density of electronic conditions we obtain:

$$E_{coh} = \frac{1}{2w(n)}\left[w^2(n)-\mu^2\right] - \nu U\,, \tag{10}$$

where $w(n)$ is semi-width of orbital non-degenerate band that depends on its filling rate;

$$w(n) = w_0(1-n\tau)\,, \tag{11}$$

w_0 is a semi-width of *s*-band, τ is a parameter of correlated hopping, $\mu = w(n)(n-1)$ – chemical potential.

Cohesion energy, calculated due to formula (10), reflects the intrinsic peculiarities of experimental dependency between cohesion energy and atomic number in *3d*-metals [1]. The dependency $E_{coh}(n)$ in *s*-band is displayed on Figure 2 ($\tau = 0{,}2$, $\frac{\mathrm{U}}{w_0} = 0{,}4$).

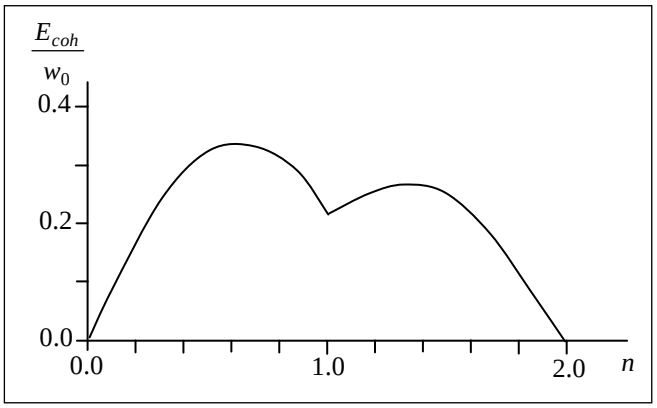

Figure 2. The dependencies of cohesive energy on filling of the s-band.

Due to the empiric links between melting temperature and cohesion energy, –

$$T_m \approx \frac{0{,}04E_{coh}}{k}, \tag{12}$$

where k – Boltzmann constant, it is obvious that Figure 2 generally reflects the dependency $T_m(n)$, as it is displayed on Figure 1.

Let us widespread the mentioned above investigation on quintuple orbital extinct band.

Cohesion energy will be as follows

$$E_{coh} = \int_{-w}^{\mu} \varepsilon\rho(\varepsilon)d\varepsilon - \nu U_{eff}, \tag{13}$$

where $\rho(\varepsilon)$ is density of electronic conditions with an eye on orbital degenerate, μ – is derived due to concentration of *d*-electrons

$$n_d = \int_{-w}^{\mu} \rho(\varepsilon)d\varepsilon, \tag{14}$$

and νU_{eff} – generalized the corresponding image of *s*-band model; here U_{eff} indicates the efficient internal atomic interaction including both Coulomb and internal Hound atomic exchange interaction.

Due to Friedel

$$\rho(\varepsilon) = \frac{5}{w(n)}, \tag{15}$$

where $w(n)$ is a semi-width of 3*d*-band, which depends on band filling rate. Then

$$\mu = \frac{w(n)n_d}{5} - w(n) \tag{16}$$

so

$$E_{coh} = 10w(n)\left(\frac{n_d}{10} - \left(\frac{n_d}{10}\right)^2\right) - \nu U_{eff}\,. \qquad (17)$$

For the further analysis we accept that in case $n_d < 5$ (Sr, Ti, V, Cr) the values $w(n)$ and U_{eff} have the same values (w_1 і U_1). We accept that reduction of delocalization energy with "polar" conditions can be represented as

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

The internal atomic interaction here was taken into account in Hartree-Fock approximation (n_d <5), ν_1 – concentration of "polar" $3d^{n+1}$– conditions.

In case $n_d > 5$ (Fe, Co, Ni) the values $w(n)$ and U_{eff} are relevant to w_2 and U_2, and formula (18) to

$$\nu_2 U_{eff} = \left(5 - n_d + 5\left(\frac{n_d}{10}\right)^2\right)U_2 \qquad (19)$$

(complying to electron-hole symmetry); here ν_2 is a concentration of "hole" $3d^{n-1}$– states.

Thus, the cohesion energy in this case is:

$$\frac{E_{coh}}{10w_2} = n_d\left(\frac{1}{10} + \frac{U_2}{10w_2}\right) - \left(\frac{n_d}{10}\right)^2\left(1 + \frac{U_2}{2w_2}\right) - \frac{U_2}{2w_2}\,. \qquad (20)$$

In case $n_d > 5$ we accept that

$$w_1 = w_2,\ U_1 = U_2,$$

two symmetric parabolic dependencies are obtained $E_{coh}(n_d)$ (for values $n_d > 5$ and $n_d < 5$).

Trustworthy $w_2(n) < w_1(n)$ [7, table 20.5], so we have two asymmetric dependencies $E_{coh}(n)$, shifted relatively to band semi-filling.

Let us make the detailed analysis of n_d =5 (Mn). Although in *Cr* and *Mn* the atomic 3*d*-conditions are filled equally, the widths of 3*d*-bands in these metals substantially differ; due to [7, Table 20.5] 5,60 eB and 6,56 eB correspondingly for Mn and Cr. It explains the lower level of cohesion energy in Mn, than in Cr; the values of efficient internal atomic interaction in both cases can be considered to be the same.

Thus, the model investigates the nature of double-hump dependency of cohesion energy from atomic number in transitive 3*d*-metals [1], as well as special features of E_{coh} for Mn.

Melting temperature. Obtained formulas for cohesion energy facilitate investigating of melting temperature dependency from 3*d*-conditions filling rates in the studied model.

Due to formula (12) for non-dimensional melting temperatures

$$\theta = \frac{kT_m}{0{,}4w} \qquad (21)$$

we obtain:

$$\theta_1 = \frac{n_d}{10} - \left(\frac{n_d}{10}\right)^2 \left(1 + \frac{U_1}{2w_1}\right) \tag{22}$$

($n_d < 5$),

$$\theta_2 = n_d \left(\frac{1}{10} + \frac{U_2}{10w_2}\right) - \left(\frac{n_d}{10}\right)^2 \left(1 + \frac{U_2}{2w_2}\right) - \frac{U_2}{2w_2} \tag{23}$$

($n_d > 5$). Additionally we will state that n_d is determined with atomic values of $3d^n$-conditions of corresponding metals. In case n_d=5 one has to take into consideration the mentioned above remarks concerning cohesion energy in Mn.

Let us have a look at the consequences of last formulas.
Formula (22) shows that maximum θ_1 exists at

$$n_d = \frac{10w_1}{2w_1 + U_1}. \tag{24}$$

It is clear that considering of internal atomic interaction shifts the maximum θ_1 leftwards from band center (due to Friedel theory maximum θ_1 would be located in the band center). The surveyed dependency maximum $T_m(n)$ (Figure 1) is relevant to vanadium. In our model it is n_d=3. Due to the formula (24) the sequence with an experiment will be at

$$U_1 = \frac{4w}{3}.$$

If one takes $2w_1 \approx 6{,}8$ eB (model [7, Table 20.5] and experimental value [1] for vanadium band width are close to each other), than $U_1 \approx 4{,}5$ eB.

The evaluation of melting temperature for vanadium due to formulas (22) and (24) gives

$$T_m \approx 2{,}4 \cdot 10^3 \text{ K},$$

That is close to observed one (Figure 1).

Making the further analysis being similar to dependency $E_{coh}(n)$, one can state that formulas (22-23) allow interpretation of observed correlation between melting temperature and 3*d*-band filling rate.

Conclusions. The author suggested the model to describe 3*d*-subsystems of transitive 3*d*-metals and their alloys for interpretation of dependency of cohesion energy and melting temperature of *3d*-metals from their atomic number.

There was shown the explanation of surveyed cohesion energy and melting temperature of *3d*-metals. The nature of two "parabolic dependencies" between cohesion energy and *3d*-band filling rate (the series Sr-Ti-V-Cr-Mn i Mn-Fe-Co-Ni) was shown as well as peculiarities linked to Mn.

One should mention that for more complete comparison of suggested theory with experimental data for *3d*-metals it is necessary to take into consideration the contribution of s-electrons and specify the value $w(n_d)$ and experimental data about *3d*-band filling rate in transitive *3d*-metals. The separate research project will be devoted to it.

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ІНТЕРПРЕТАЦІЯ ЗАЛЕЖНОСТІ ЕНЕРГІЇ КОГЕЗІЇ ТА ТЕМПЕРАТУРИ ПЛАВЛЕННЯ ПЕРЕХІДНИХ 3D-МЕТАЛІВ ВІД АТОМНОГО НОМЕРА

Леонід Дідух

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***Резюме**. Запропоновано модель для опису особливостей залежності енергії зв'язку та термодинамічних характеристик 3d-металів від атомного номера. Отримані результати пояснюють експериментальні залежності енергії зв'язку й температур плавлення 3d-металів від атомного номера: «аномалію» для Mn і дві нееквівалентні «параболічні залежності».*

***Ключові слова**: перехідні 3d-метали, температура плавлення, точка плавлення, енергія когезії, атомний номер, орбітальна зонна енергія, прямокутна густина станів, внутрішньоатомні взаємодії, вузол.*

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