

INVESTIGATION OF THERMODYNAMIC PROPERTIES OF LIQUID TRANSITION METALS

NGHIÊN CỨU MỘT SỐ TÍNH CHẤT NHIỆT ĐỘNG HỌC CỦA CÁC KIM LOẠI CHUYỂN TIẾP LỎNG

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ABSTRACT

We present a study of thermodynamic properties of liquid transition metals. The cohesive energies and the heats of fusion have been calculated in the bond-order approach coupled with the cluster Bethe lattice method for 3d, 4d and 5d liquid transition metals, taking in account s-d hybridization which is treated self-consistently. The results of the heats of fusion are in good agreement with experimental data. An analyze of the contributions related to the s- and d-electrons to the cohesive energies are realized and showed that s-electrons play an important part in the cohesion of liquid transition metals. The trends of thermodynamic properties for three series have been also discussed. So far, our work is the first systematic study of properties of cohesion of all the transition metals in their liquid phases.

TÓM TẮT

Bài báo nghiên cứu một số tính chất nhiệt động của các kim loại chuyển tiếp lỏng. Năng lượng liên kết và nhiệt nóng chảy của các kim loại dãy 3d, 4d và 5d được tính toán trong phép gần đúng “bậc liên kết” kết cặp với phương pháp mạng Bethe, có tính đến sự lai hoá giữa các điện tử s và d. Các kết quả về nhiệt nóng chảy phù hợp tốt với thực nghiệm. Các tác giả phân tích sự tham gia vào năng lượng liên kết của chất lỏng từ các điện tử s và điện tử d và nhận xét rằng phần đóng góp của các điện tử s là quan trọng, nhất là đối với các kim loại quý (noble metals), và thêm nữa, cần tính đến sự lai hoá của các điện tử s và d. Bài báo cũng thảo luận về các khuynh hướng tiến triển của các tính chất nhiệt động trên trong ba dãy kim loại chuyển tiếp. Cho đến nay công trình của các tác giả là công trình đầu tiên nghiên cứu một cách hệ thống các tính chất liên kết trong các kim loại chuyển tiếp lỏng.

I. INTRODUCTION

The strict theory of simple liquid metals is rather well developed. Existing methods allow one to investigate successfully the simple metal liquids and also their binary alloys.

For liquid of transition metals and their alloys, the situation is much poorer. The investigations of liquid transition metals in the frameworks of electron theory and the theory of liquids started from the work of Aryasetiawan *et al* [1]. In this work, the variational method of thermodynamic perturbation theory (TPT) with a hard-sphere (HS) reference system was used. Further development of the theory deals with the Wills–Harrison (WH) approximation [2], mainly applied by Hausleitner and Hafner [3] and Ab initio molecular dynamics [4,5]. Recent works on liquid transition metals calculated structural

and thermodynamic characteristics of some liquid transition metals by using the Oli local modified potential [6]. Most recently, S. S. Dalgic [7] have calculated structure properties of liquid FCC transition metals using the embedded atom method.

So far, any work haven’t studied systematically the three series of transition metals in their liquid phases. In the paper [8], we have presented an approach to study 3d-liquid transition metals and their alloys. This approach allows an explicit expression of the interatomic potentials called “bond-order” potentials.

In this paper, we investigated the thermodynamic properties of the liquid transition metal, such as cohesive energies and heats of fusion for 3d-, 4d-, and 5d-series transition metals. To do that, we have constructed the interatomic potential in the

same bond-order potential model as described in [8] and we have used them in molecular dynamics simulations in order to obtain the liquid states of the metals.

To the best of our knowledge, the work presented below is the first systematic study of properties of cohesion of all the transition metals in their liquid phases.

II. MOLECULAR DYNAMICS SIMULATIONS

We have used our interatomic interactions potentials in a micro-canonical NVE molecular dynamic (MD) investigation of liquid transition metals.

We consider a system of 1332 atoms in a cubic box with periodic boundary condition, such that the atomic density of the system is equal to the experimental value.

The liquid is then obtained by raising the initial temperature of the system and subsequently scaled down to the required value. The Newtonian equations of motion were solved using the velocity form of the Verlet algorithm with a time increment of $3 \cdot 10^{-15}$ s. Classical dynamic trajectories of 10^4 time steps were generated to calculate properties of the liquids.

III. RESULTS AND DISCUSSIONS

In this paper, we have calculated the cohesive energies and the heats of fusion for 3d-, 4d-, and 5d-series transition metals. The cohesive energy related to orbital α ($\alpha = s, d$) on the site i is written by definition as:

$$E_{coh}^{\alpha(i)} = \int_{-\infty}^{E_F} (E - E_{\alpha}^0) n_{\alpha(i)}(E) dE \quad (1)$$

where E_{α}^0 is the atomic energy level of orbital α , E_F is Fermi level, $n_{\alpha(i)}(E)$ is the local density of electronic states (LDOS) of the orbital α at the site i . The LDOS can be determined as the imaginary part of the Green function. In disordered systems such as liquids, we are interested only in configuration-averaged values, therefore to calculate these quantities, we have used the scalar cluster Bethe

lattice method (SCBLM) [8]. The total cohesive energy comes from the contribution of electrons s and d :

$$E_{coh}^{total} = E_{coh}^{(s)} + E_{coh}^{(d)} \quad (2)$$

The heat of fusion is then evaluated as the difference of cohesive energies of the metal in its crystal phase and liquid phase at the melting temperature:

$$L_f = E_{coh}^{solid} - E_{coh}^{liquid} \quad (3)$$

Table 1. Input data for MD simulations

Series	Element	T _{fusion} (°C)	ρ (Å ⁻³)	E _d ⁰ (eV)
3d-	Sc	1541	0.038	7.05
	Ti	1668	0.052	7.76
	V	1910	0.065	8.13
	Cr	1907	0.073	8.01
	Mn	1246	0.065	7.91
	Fe	1538	0.075	7.64
	Co	1495	0.079	7.36
	Ni	1445	0.080	6.91
4d-	Cu	1084	0.076	5.90
	Y	1526	0.029	6.75
	Zr	1855	0.038	7.17
	Nb	2477	0.050	7.29
	Mo	2623	0.059	7.12
	Tc	2157	0.068	6.67
	Ru	2334	0.063	6.02
	Rh	1964	0.063	5.08
5d-	Pd	1554	0.059	4.52
	Ag	961	0.052	2.49
	La	920	0.024	4.69
	Hf	2233	0.040	9.12
	Ta	3017	0.050	9.50
	W	3422	0.058	9.45
	Re	3186	0.061	8.99
	Os	3033	0.063	8.38
	Ir	2466	0.060	7.35
	Pt	1768	0.061	6.51
	Au	1064	0.053	5.18

We have calculated E_{coh}^{liquid} and E_{coh}^{solid} from equation (1) on the same basis, i.e. using SCBLM formalism coupled with the same tight-binding Hamiltonian.

In Table 1 are presented the input data used for MD simulations: temperature of

fusion T_{fusion} , experimental atomic densities of the liquid phases ρ and atomic energy levels of the orbital d , E_d^0 (relative to atomic energy level of orbital s , i.e. putting $E_s^0 = 0$).

Table 2. Total cohesive energies and contributions come from s - and d - electrons in the liquids

Series	Element	$-E_{\text{coh}}^{(s)}$ (kJ/mol)	$-E_{\text{coh}}^{(d)}$ (kJ/mol)	$-E_{\text{coh}}^{\text{total}}$ (kJ/mol)
3d-	Sc	120	490	611
	Ti	184	642	826
	V	273	821	1094
	Cr	384	878	1262
	Mn	302	621	923
	Fe	368	544	912
	Co	349	370	719
	Ni	396	224	620
	Cu	420	62	482
4d-	Y	103	610	713
	Zr	163	820	983
	Nb	253	1033	1286
	Mo	335	1114	1449
	Tc	428	1089	1516
	Ru	374	760	1134
	Rh	369	496	865
	Pd	353	259	612
	Ag	339	92	431
5d-	La	160	542	702
	Hf	215	994	1209
	Ta	219	1167	1386
	W	286	1223	1510
	Re	322	1083	1404
	Os	351	878	1229
	Ir	317	527	843
	Pt	374	301	675
	Au	377	131	507

The calculated results for cohesive energies of liquid transition metals are presented in Fig. 1 and in Table 2. It follows that the cohesive energy $E_{\text{coh}}^{\text{total}}$ of transition metals exhibits extreme behavior and has a minimum for Cr, Tc and W.

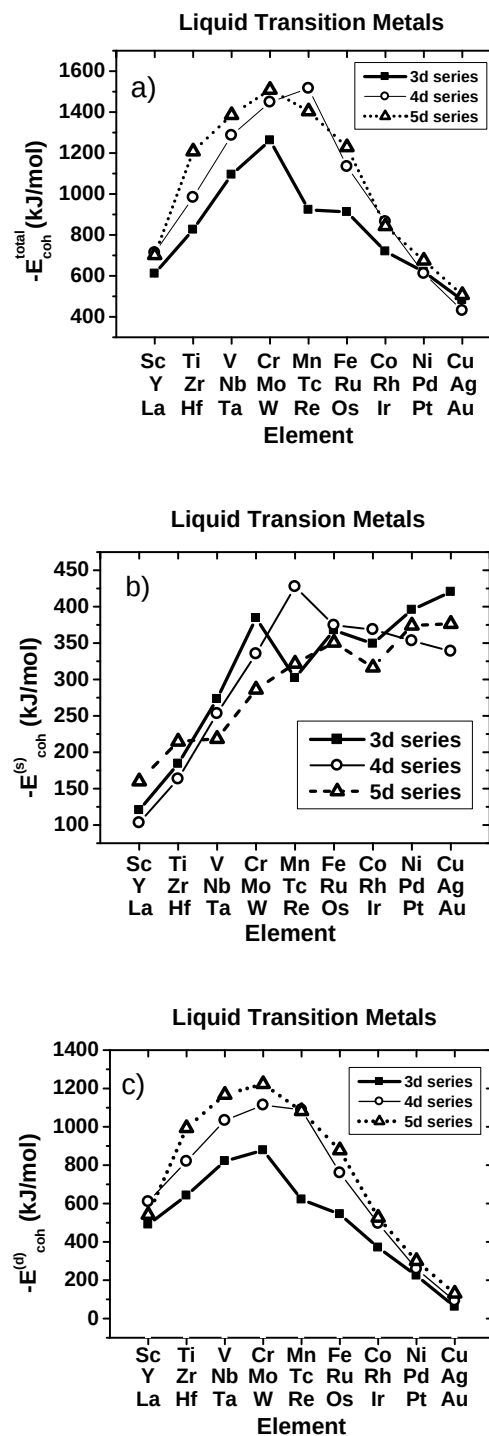


Fig.1 Cohesive energies of liquid transition metals (a- $E_{\text{coh}}^{\text{total}}$, b- $E_{\text{coh}}^{(s)}$, c- $E_{\text{coh}}^{(d)}$)

These minima are associated with the maximum negative contributions of $E_{\text{coh}}^{(d)}$ for chrome and tungsten in each of the corresponding transition series and with the

very negative value of $E_{coh}^{(d)}$ for technetium. According to Eq. (1), such values of $E_{coh}^{(d)}$ are due to the fact that the d -bands of chrome, technetium, and tungsten are almost half-complete. It is showed from Fig. 1 that the term $E_{coh}^{(d)}$ has a predominant contribution to the total cohesive energy E_{coh}^{total} for the majority of transition metals. In each of the transitive series, $E_{coh}^{(d)}$ decreases for metals of the eighth group and becomes very small for noble metals. The contribution of s -electrons, $E_{coh}^{(s)}$, to the total cohesive energy E_{coh}^{total} is, like in the solid phase [9], considerable, and it is an important source of cohesive force in noble metals. Fig. 1b indicates that $E_{coh}^{(s)}$ varies non-monotonically within the transition series. It is minimum in absolute magnitude for the metals at the beginning of the transition series and increases to the end of the series.

One of the greatest successes of our model has been in explaining the trends in the cohesive energies of the liquid transition metals. The 4d and 5d transition metals have a large cohesive energy which varies in a regular way across the series while the 3d transition metals, however, show a pronounced deviation from this behavior. This departure from the roughly parabolic variation observed in the 4d and 5d series begins at Mn, and decreases in magnitude as the band is filled further, Ni having properties similar to those of Pd and Pt. In the middle of the 3d series, therefore, the d electrons seem to be prevented from participating fully in the bonding.

Further support for this conclusion comes from the variation of atomic volume in the liquid, which would be expected to decrease with increasing binding strength. In the 4d and 5d series, the atomic volume decreases smoothly as the band becomes half filled, and then increases as the band is filled further. In the 3d series, however, Fe and Co have an atomic volume larger than that of Ni. This behavior can be understood by studying the influence of the effect of electron interactions in the systems which is greatest for a half-filled band and of crucial importance for 3d series

where the bandwidth is smaller than in 4d and 5d series.

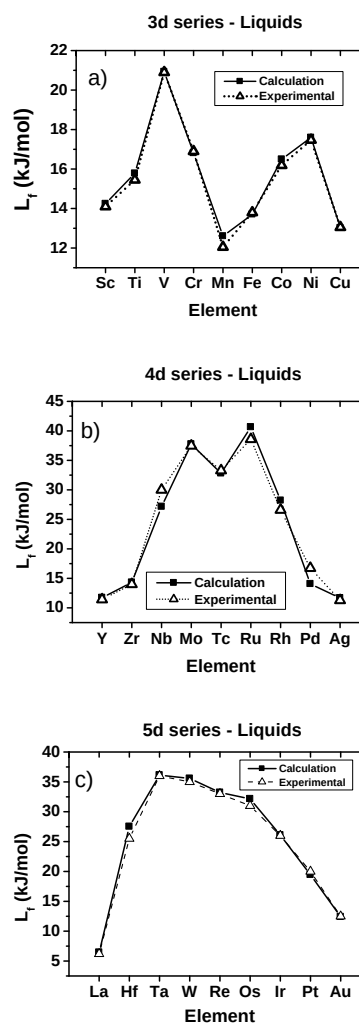


Fig.2 Heat of fusion of transition metals (a- 3d series, b- 4d series, c- 5d series)

An important characteristic of the strength of interatomic bonds is the fusion heat L_f , which is equal to the energy needed to transform one mole of solid substance into liquid phase. The theoretical results of the L_f for three series are presented in Fig. 2. They are in very good agreement with the experiment (Periodic Table) and therefore showed the validity of the model in which our interaction potentials are constructed. Fig. 3 shows the heats of fusion of liquid transition metals as a function of the cohesive energies. It should be noted that the strong correlation between these quantities allows us to consider the cohesive energy as a physical constant characterizing the strength of cohesive forces in metal.

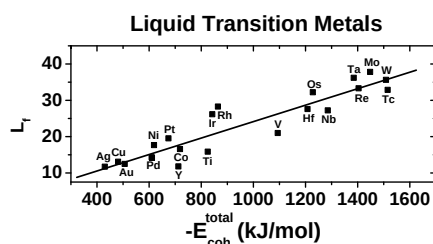


Fig.3 Dependence of heats of fusion on the cohesive energies

Another interesting aspect is the role played by s-d hybridization in the cohesive energy of the liquid transition metal systems. In this work, this contribution to the total bond energy has been estimated of about 25-74% across the series and displayed for illustration for 4d-series in Table 3.

Table 3. Role played by s-d hybridization in the cohesion energy of 4d-series liquids

Element	$-E_{coh}^{s-d}$ (kJ/mol)	$-E_{coh}^{total}$ (kJ/mol)	$E_{coh}^{s-d} / E_{coh}^{total}$
Y	178	713	0.25
Zr	300	983	0.31
Nb	443	1286	0.35
Mo	544	1448	0.38
Tc	607	1516	0.40
Ru	586	1134	0.52
Rh	538	865	0.62
Pd	450	611	0.74
Ag	169	430	0.39

IV. CONCLUSIONS

We have used the bond-order approach coupled with the tight-binding cluster Bethe lattice method to calculate the cohesive energies of liquid transition metals and its s- and d-electron contributions. The heats of fusion have been also estimated, they have been compared with the experimental data and showed a very good agreement with these ones. As the properties of transition metals associated with the interatomic interaction in crystals, it should be pointed out that they are strongly correlated with the cohesive energy. In passing from the third to the fifth series, the cohesive energy increases, which is consistent with the observed tendency to increase in their refractoriness and strength of interatomic bonds and may again be associated with the structure of the d-bands, namely, with their width. It should be noted that $E_{coh}^{(d)}$ plays a decisive, but not unique role in the formation of the cohesive force. Hence, the effect of the s-electrons and the hybridization of electrons s and d should be taken into account as a factor affecting the strength of transition metals.

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