Melting points and chemical bonding properties of 3d transition metal elements

Wataru Takahara

Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan

E-mail: takahara@mapse.eng.osaka-u.ac.jp

Abstract. The melting points of 3d transition metal elements show an unusual local minimal peak at manganese across Period 4 in the periodic table. The chemical bonding properties of scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel and copper are investigated by the DV-Xα cluster method. The melting points are found to correlate with the bond overlap populations. The chemical bonding nature therefore appears to be the primary factor governing the melting points.

1. Introduction

In general, the melting points of transition metals are much higher than those of main-group metals. The outermost as well as inner shell electrons contribute to the bonding in transition metals. Across Period 4 in the periodic table, the melting points of 3d transition metal elements show a maximal peak around vanadium and chromium. Further, the melting points decrease from chromium to copper and zinc. However, the melting points show a local minimal peak at manganese. This behavior is not entirely clear although there have been attempts to explain the anomaly [1, 2].

In the present work, the chemical bonding properties of scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel and copper are investigated by the DV-Xα cluster method to clarify the local minimal peak at manganese.

2. Computational method

DV-Xα molecular calculations were carried out using the SCAT code developed by Adachi et al. [3]. The calculations were based on the Hartree-Fock-Slater approximation with an exchange correlation between electrons based on the Slater local exchange-correlation potential \( V_{xc} \) given by

\[
V_{xc} = -3\alpha \left( \frac{3}{8\pi} \rho(\mathbf{r}) \right)^{1/3},
\]

where \( \rho(\mathbf{r}) \) is the local electron density at position \( \mathbf{r} \) [2-4]. In this calculation, \( \alpha \) is fixed at a constant value of 0.7, and the self-consistent charge approximation is employed. The molecular orbital wave function \( \phi \) is expressed by a linear combination of atomic orbitals (LCAO) as

\[
\phi_i = \sum_l C_{il} \chi_l,
\]

where \( C_{il} \) is the coefficient and \( \chi_l \) is a basis function. Numerical atomic orbitals are employed as the basis functions in the DV-Xα method.

Figure 1 shows the model clusters analyzed in the present work. Sc\(_{19}\) cluster is based on a hexagonal close-packed (hcp) crystal structure. Ti\(_{27}\), V\(_{27}\), Cr\(_{27}\), Mn\(_{27}\) and Fe\(_{27}\) clusters are based on...
body-centered cubic (bcc) crystal structures. Co\(_{19}\), Ni\(_{19}\) and Cu\(_{19}\) clusters are based on face-centered cubic (fcc) crystal structures. The atomic distances of these clusters are determined from the high temperature crystal structure data near the melting points [5, 6]. Table 1 lists the high temperature crystal structure data for cluster modeling. Sc\(_{19}\) cluster is based on the hcp crystal structure at 1773K, where lattice constants \(a = 0.3368\) nm and \(c = 0.5366\) nm [5]. Ti\(_{27}\), V\(_{27}\), Cr\(_{27}\), Mn\(_{27}\) and Fe\(_{27}\) clusters are based on bcc crystal structures at 1670K, 1773K, 1773K, 1413K and 1781K, where lattice constants are 0.33338 nm [5], 0.30850 nm [5], 0.2936 nm [5], 0.350 nm [6] and 0.29396 nm [5], respectively. Co\(_{19}\), Ni\(_{19}\) and Cu\(_{19}\) clusters are based on fcc crystal structures at 1671K, 1473K and 1343K, where lattice constants are 0.36214 nm [5], 0.35987 nm [5] and 0.3692 nm [5], respectively. DV-X\(\alpha\) molecular calculations are performed for these model clusters. The atomic positions are fixed in the calculations for all the cluster models. The atomic basis functions used in the present calculations are 1s-4p for Sc-Cu. No point groups are used to produce symmetry orbitals. Self-consistency within 0.001 electrons is obtained for the final orbital populations. Non-spin-polarized cases are considered in the molecular orbital calculations.

![Figure 1. Hcp, bcc, and fcc based cluster models.](image)

**Table 1.** Hcp, bcc, and fcc based cluster models.

| Atomic number | Element | Melting point, MP (K) | Reference temperature for modeling, RT (K) | Based crystal structure (high temperature phase) | Lattice constants (nm) | RT/MP |
|---------------|---------|-----------------------|-------------------------------------------|-----------------------------------------------|-----------------------|-------|
| 21            | Sc      | 1812                  | 1773                                      | hcp                                           | \(a=0.3368\) \(c=0.5366\) | 0.98  |
| 22            | Ti      | 1939                  | 1670                                      | bcc                                           | 0.33338               | 0.86  |
| 23            | V       | 2190                  | 1773                                      | bcc                                           | 0.30850               | 0.81  |
| 24            | Cr      | 2130                  | 1773                                      | bcc                                           | 0.2936               | 0.83  |
| 25            | Mn      | 1519                  | 1413                                      | bcc                                           | 0.350                | 0.93  |
| 26            | Fe      | 1809                  | 1781                                      | bcc                                           | 0.29396              | 0.98  |
| 27            | Co      | 1768                  | 1671                                      | fcc                                           | 0.36214              | 0.95  |
| 28            | Ni      | 1728                  | 1473                                      | fcc                                           | 0.35987              | 0.85  |
| 29            | Cu      | 1358                  | 1343                                      | fcc                                           | 0.3692              | 0.99  |
Mulliken population analysis [7] is employed for evaluating the bond overlap population [2-4, 8]. The bond overlap population, $Q_{AB}$, is defined as

$$ Q_{AB} = \sum_{i \in A, j \in B} Q_{ij} $$

where

$$ Q_{ij} = \sum_i Q_{i}^1 $$

$$ Q_{ij}^1 = f_i C_{ii} C_{jj} S_{ij} $$

$$ S_{ij} = \int \chi_i^* \chi_j dv $$

here $S_{ij}$ is called the overlap integral in the LCAO molecular orbital method [3, 4, 8], $f_i$ is the occupation number of the $i$th molecular orbital, and $Q_{ij}^1$ is the overlap population between atomic orbitals $i$ and $j$ [4, 8]. The bond overlap population $Q_{AB}$, which is defined as the sum of $Q_{ij}$ over all $i$ belonging to atom A and all $j$ belonging to atom B, is considered the measure of strength of covalent bonding between atoms A and B [4, 8].

3. Results and discussion

Figure 2 shows the bond overlap population between the central metal atom and neighboring metal atoms in the Sc$_{19}$, Ti$_{27}$, V$_{27}$, Cr$_{27}$, Mn$_{27}$, Fe$_{27}$, Co$_{19}$, Ni$_{19}$, and Cu$_{19}$ clusters. The melting points of these elements are also plotted in the figure. The filled circles show the bond overlap populations and the open circles show the melting points. The bond overlap population was derived from the DV-X$\alpha$ orbitals in the calculations considering only the X$\alpha$ exchange correlation, without electron correlation. Although the finer details with respect to energy are rather sensitive to the way electron correlation is included, information concerning the wave functions is insensitive to electron correlation and such DV-X$\alpha$ calculations can be considered reliable [8-12]. Both the bond overlap populations and the melting points show the local minimal peak at manganese. As the bond overlap population is the measure of the strength of covalent bonding, the local minimal peak of the bond overlap population at manganese indicates the relative weakening of the chemical bonding of manganese compared to the two-sided elements, chromium and iron.

![Figure 2. Bond overlap population between the central metal atom and neighboring metal atoms in the Sc$_{19}$, Ti$_{27}$, V$_{27}$, Cr$_{27}$, Mn$_{27}$, Fe$_{27}$, Co$_{19}$, Ni$_{19}$, and Cu$_{19}$ clusters. Melting points of these elements are also plotted.](image-url)
In the transition metals, the changes such as melting points are often associated with the number of d-electrons, $n_d$. In the simple Friedel model, the peak is at $n_d = 5$, for half-filled d-shell. However, this is not the case at manganese [1]. There have been attempts to explain the anomaly at manganese with account of the correlation effect [1]. In contrast, the present calculations consider only Xα exchange correlation, without electron correlation. Further, non-spin-polarized cases are considered in the present calculations. Although the unusual behavior of manganese is often discussed in connection with the magnetic properties, the chemical bonding nature appears to be the primary factor governing the melting points.

4. Conclusions
Chemical bonding properties of 3d transition metal elements, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel and copper, are investigated by the DV-Xα cluster method. The bond overlap populations show a local minimal peak at manganese. The calculations consider only Xα exchange correlation, without electron correlation, and only non-spin-polarized cases. The chemical bonding nature appears to be the primary factor governing the anomaly of melting point at manganese.

Acknowledgments
The computation was partially carried out using the computer facilities at Cybermedia Center, Osaka University and at Research Institute for Information Technology, Kyushu University.

References
[1] Irkhin V Yu and Irkhin Yu P 2007 *Electronic structure, correlation effects and properties of d- and f-metals and their compounds* (Cambridge International Science Publishing)
[2] Adachi H 1997 *Adv. Quant. Chem.* 29 49
[3] Adachi H, Tsukada M and Satoko C 1978 *J. Phys. Soc. Jpn.* 45 875
[4] Adachi H 1997 *Mater. Trans., JIM* 38 485
[5] Villars P and Calvert L D 1991 *Pearson's Handbook of Crystallographic Data for Intermetallic Phases* Second Edition (Materials Park, OH: ASM International)
[6] Asada T and Terakura K 1993 *Phys. Rev. B* 47 15992
[7] Mulliken R S 1955 *J. Chem. Phys.* 23 1833
[8] Adachi H 2006 *Hartree-Fock-Slater Method for Materials Science*, The DV-Xα Method for Design and Characterization of Materials, ed H Adachi, T Mukoyama and J Kawai (Springer-Verlag Berlin Heidelberg) p 3
[9] Morinaga M, Murata Y and Yukawa H 2006 *Hartree-Fock-Slater Method for Materials Science*, The DV-Xα Method for Design and Characterization of Materials, ed H Adachi, T Mukoyama and J Kawai (Springer-Verlag Berlin Heidelberg) p 23
[10] Morinaga M, Nasu S, Adachi H, Saito J and Yukawa N 1991 *J. Phys.: Condens. matter* 3 6817
[11] Takahara W, Maeda H and Minami F 2003 *Adv. Quant. Chem.* 42 275
[12] Takahara W 2012 *J. Phys.: Conf. Ser.* 379 012040