

On the Roles of Interatomic Interactions and Coordination Numbers on Einstein Temperatures of 3D Transition Metals

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أدوار التفاعلات بين الذرات والأرقام التنسيقية على درجة حرارة «أينشتين» للمعادن الإنتقالية ثلاثية الأبعاد

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خلاصة: لقد قمنا بدراسة أدوار الأرقام التنسيقية والتفاعلات بين الذرات على درجة حرارة «أينشتين» θ_E لعدد من المعادن الإنتقالية ثلاثية الأبعاد. استخدمنا بعض الجهود شبه الكامنة لمعادن إنتقالية معروفة في الحسابات التي تهدف إلى المقارنة بين أدوار هذه الجهود شبه الكامنة على درجة حرارة «أينشتين». يظهر دور الذرات المجاورة على درجة الحرارة كنتيجة ثانوية على هذه الحسابات.

ABSTRACT: We have investigated the roles of the coordination numbers and interatomic interactions on the Einstein temperatures θ_E for a number of bcc 3d transition metals. We have employed a few of the popular transition metal pseudopotentials in the calculations aiming at a comparative survey of the roles of these pseudopotentials on the Einstein temperature; the role of the neighbouring atoms on the latter emerges as a by-product of the calculations.

Over the last two decades there have been numerous calculations aiming to investigate the cohesive and thermodynamic (Pettifor, 1983; Hafner, 1987; Young, 1992) properties of metals and alloys in terms of the pairwise interatomic interactions involved in the global energetics. Among many other applications, the calculations of the thermomechanical properties, e.g. Einstein temperatures θ_E in terms of pair potentials, have drawn much interest (Rahman and Salek, 1992) in recent years. Because of certain obvious reasons, the major bulk of the available calculations were aimed at the simpler systems. With the advent of the realistic forms of pair interactions (Wills and Harrison, 1983; Finnis and Sinclair, 1984; Bretonnet and Silbert, 1992), however, there have been a number of calculations on the transition metals (Karaoglu and Rahman, 1994). Even though the basis of these transition metal interatomic potentials is the so called force-theorem (Mackintosh and Andersen, 1980) controlling the cancellation between relaxations in the one particle potential and self-energy corrections, the decompositions of the potentials can be achieved in various ways. Whatever the mode of decomposition might be, the effective pair potential can be profitably written as a sum of the interactions arising from the screened Coulomb repulsion, the bond bending contribution and a repulsive contribution inherent to the

shift of the centre of the d-band. Concurrently a trend based on the multi-ion interactions ((Finnis and Sinclair, 1984) and the d-phase shift (Bretonnet and Silbert, 1992) has been broadly successful in calculating the various structural and thermodynamic properties of transition metals.

It is relevant to mention here that since most of the structural and thermodynamic properties are global in nature, the average profile, and not any specific detail of the pair potential, is of vital importance for these cases. On the other hand, since the differential derivatives of the pair potentials at the lattice vector positions are involved in calculating the Einstein temperature, any fine details of the pair potentials at every relevant point is equally important. In particular the profile of the pair potential at the first lattice vector is of specific importance in this special situation; this is because the major contribution of θ_E comes from the nearest neighbours for almost all of the systems. The present attempt enabled us to look at these aspects.

Formulations and Calculations

The main ingredients in the present calculation are the pair potentials $\phi(r)$ due to Wills and Harrison (WH), 1983, Finnis and Sinclair (FS), 1984 and Bretonnet and Silbert (BS), 1992. Once the pair potential is known, it can be

related to the Einstein temperature at a temperature T as follows (Hasegawa and Young, 1980):

$$\frac{3M}{\hbar^2} [k_B \theta_E(T)]^2 = \sum_{R \neq 0} [\nabla^2 \phi(r)]_R \quad (1)$$

where M is the ionic mass, k_B the Boltzmann constant and R is a lattice vector of the underlying lattice. For spherically symmetric approximation we write

$$\theta_E^2(T) = \frac{1.823 \times 10^7}{W} \sum_{R \neq 0} \left(\frac{d^2 \phi}{dr^2} + \frac{2}{r} \frac{d\phi}{dr} \right)_R \quad (2)$$

where W is the atomic weight of the element. The differential terms in eq. (2), i.e.,

$$g = \left(\frac{d^2 \phi}{dr^2} \right)_R, \quad T = \left(\frac{1}{r} \frac{d\phi}{dr} \right)_R \quad (3)$$

are respectively known as the radial and tangential force constants. The experimental Einstein temperature θ_{exp} is deduced from the experimental entropy S_{exp} (Hultren et al. 1973) through the approximate relation

$$S_{\text{exp}}(T) = 3k_B \left\{ \frac{\theta_E/T}{e^{\theta_E/T} - 1} - \ln(1 - e^{-\theta_E/T}) \right\} \quad (4)$$

The input parameters in calculating the various forms of $\phi(r)$ at room temperature have been obtained from Wills and Harrison, 1983, Finnis and Sinclair, 1984 and Bretonnet and Silbert, 1992, respectively. The calculated $\phi(r)$ s for Cr are shown in Figure 1. The profiles of these pair potentials in the regions of interest are remarkably distinct. The deep minimum in the WH- $\phi(r)$, attributed almost entirely to the d-d matrix element, supercedes those appearing in the other

two. The shallow minimum in the BS- $\phi(r)$ is on the other hand a reflection of the predominant sp contribution over the d-contribution arising from the inverse scattering mode. The FS- $\phi(r)$ representing a simple form of the multi-ion interactions is apparently seen as an 'average' of the two other pair potentials. A similar trend is noticed in the pair potentials of the other 3d transition metals concerned.

Results and Discussion

The values of the Einstein temperature θ_E for V, Cr, Mn and Fe as calculated from the various pair potentials considering the various neighbouring contributions are presented in Table 1. Looking at these results it is noticed that for most of the systems about 80% contributions to the Einstein temperatures, irrespective of the model pair potentials, come from the nearest neighbours alone. This is a manifestation of the essence of the Einstein model that an atom vibrates independently in an averaged field (mean field) in the presence of all other atoms and consequently

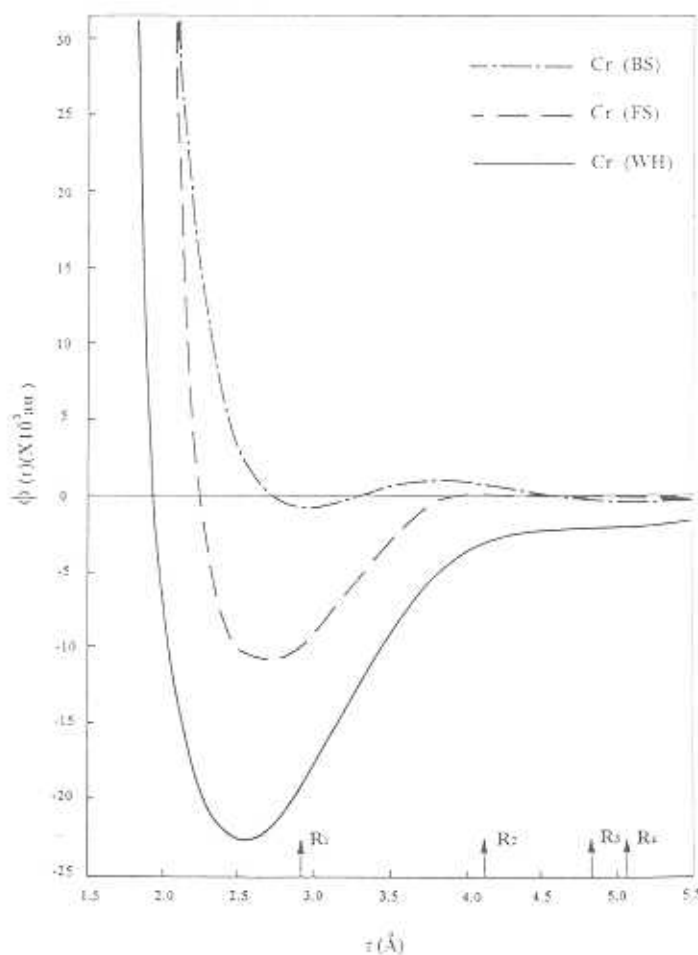


Figure 1. The pair potentials $\phi(r)$ for Cr as calculated by using the Wills-Harrison (WH), Finnis-Sinclair (FS) and Bretonnet-Silbert (BS) model potentials. The local field factor used in the calculations is due to Ichimaru and Utsumi, 1980. The input quantities used in the calculations correspond to room temperature.

the dragging effects, e.g. anharmonicities caused by any long range ordering, are secondary. Results for V, the top element of the group, are very consistent with the experimental value. For Cr, while the FS pair potential reproduces a fairly consistent value for θ_E , the WH and BS potentials visibly underestimate it. The most noticeable situation is observed in the case of Mn. While the WH and BS potentials generate very consistent values of θ_E , the FS potential totally fails to produce any real value for θ_E , the latter situation arises presumably because of the unphysical nature of the curvature of $\phi(r)$ at the relevant lattice vector positions. This gives rise to an upright tangential force constant associated with the FS pair potential in conjunction with the present prefixed bcc crystal structure. Mn, under normal thermodynamic conditions, belongs to a complex bcc (A12) prototype structure and so any consideration of such a structure may overcome the unphysical nature of the respective force constant; this remains to be looked at. For Fe, the FS pair potential seems to be relatively superior to the other two potentials even though the overall situation is within an acceptable range.

Conclusions

In the present investigation we have reported on the fine details of the profile of $\phi(r)$ at the lattice vector positions of several 3d transition metals through calculating their Einstein temperatures θ_E . The overall assessment shows that all the 3d transition-metal pair potentials reproduce these quasi-local dynamic quantities within a certain degree of consistency (except for Mn with the FS pair potential). This qualitative consistency may also lead to the conclusion that any local thermomechanical quantities, e.g. elastic constants, may also be reproduced consistently by employing these pair potentials; this is because the elastic constants are also derived from the derivatives of θ_E at only the first lattice vector position. In conclusion, we should make a critical remark that the present theoretical scheme used in the calculations is based on the harmonic approximation and semiempirical potentials, whereas the experimental results contain the effects of many-body forces, arising from the nonlinear response and the anharmonicity inherent in any solid. Work considering these points is in progress.

TABLE I

The calculated values of θ_{En} considering the various numbers of shells (denoted by n) for V, Cr, Mn* and Fe. The pair potentials (PP) used are of WHI (Wills and Harrison, 1983), FS (Finnis and Sinclair, 1984) and BS (Bretonnet and Silbert, 1992) forms. Experimental values are denoted by θ_{+exp}

Metal	PP	θ_{E1}	θ_{E2}	θ_{E3}	θ_{E4}	θ_{E5}	θ_{E6}	θ_{E7}	θ_{E8}	θ_{eq1}	$\theta_{ED}^{\#}$
V	WHI	227	268	243	259	265	262	252	247	263	253
Cr	WHI	239	282	254	259	262	261	252	242	331	307
Mn	WHI	226	255	233	237	241	239	234	231	231	267
Fe	WHI	213	234	224	237	242	239	242	234	282	280
V	FS	165	237	-	-	-	-	-	237	263	253
Cr	FS	273	364	-	-	-	-	-	364	331	307
Mn	FS	-	-	-	-	-	-	-	-	231	267
Fe	FS	218	254	-	-	-	-	-	254	282	280
V	BS	234	263	256	269	272	271	270	270	263	253
Cr	BS	244	274	268	281	284	282	278	276	331	307
Mn	BS	226	249	247	256	258	256	250	247	231	267
Fe	BS	211	228	229	237	239	239	243	238	282	280

* Mn corresponds to a complex bcc structure (Hasegawa and Young, 1980).

+ Deduced from eq.4 taking S_{exp} from Hultgren et al, 1973.

$\theta_{ED} = (2/3)\theta_D$ (Rahman and Salek, 1992), θ_D is the experimental Debye temperature (Kittel, 1996).

References

- BRETONNET, J.L. and SILBERT, M. 1992. Interatomic Interactions in transition Metals. Application to Vanadium. *Phys. Chem. Liq.* **24**, pp 169-176.
- FINNIS, M.W. and SINCLAIR, J.F. 1984. A simple empirical N-Body Potential for Transition Metals. *Phil. Mag.*, **A50**, pp 45-55.
- HAFNER, J. 1987. *From Hamiltonians to Phase Diagram (1st Edition)*. Springer-Verlag, Berlin.
- HASHIGAWA, M. and YOUNG, W.H. 1980. Elastic Constants of bcc Simple Metals. *J. Phys. F: Metal Phys.* **10**, pp 225 - 231.
- HULTGREN, R., DESAI, P.D., HAWKINS, D.T., GLEISER, M., KELLEY, K.K. and WAGMAN, D.D. 1973. *Selected Values of the Thermodynamic Properties of the Elements*. American Society for Metals, Ohio.
- ICHIMARU, S. and UTSUMI, K. 1980. Many - Electron Interactions. *Phys. Rev.* **B24**, pp 7385 - 7393.
- KARAOGLU, B. and RAHMAN, S.M.M. 1994. Thermomechanical Properties of 3d Transition Metals. *Int. J. Mod. Phys.* **8**, pp 1639 - 1654.
- KITTEL, C. 1996. *Introduction to Solid State Physics (6th Edition)*. John Wiley & Sons, Inc., New York.
- MACKINTOSH, A.R. and ANDERSEN, O.K. 1980. Band Structures of Transition Metals. In *Electrons at the Fermi Surface*, ed M. Springford, Cambridge University Press, London.
- PETTIFOR, D.G. 1983. Structures of Transition Metals. In *Physical Metallurgy*, Vol 1, eds R.W. Cahn and P-Haasen, North-Holland Publishing Co., Amsterdam.
- RAHMAN, S.M.M. and SALEK, S. 1992. Thermomechanical Properties of Certain Elemental Crystals. *Int. J. Mod. Phys.* **6**, pp 3069 - 3077.
- WILLS, J.M. and HARRISON, W.A. 1983. Interatomic Interactions in Transition metals. *Phys. Rev.* **B28**, pp 4363-4373.
- YOUNG, W.H. 1992. Structural and Thermodynamic Properties of NFE Liquid Metals and Binary Alloys. *Prog. Phys.* **55**, pp 1769-1822.

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