ADP011903

TITLE: High Temperature Properties of the Fcc Metallic Crystals in the Anharmonic Approximation

This paper is part of the following report:

TITLE: International Conference on Solid State Crystals 2000: Growth, Characterization, and Applications of Single Crystals Held in Zakopane, Poland on 9-12 October 2000

To order the complete compilation report, use: ADA399287

High temperature properties of the fcc metallic crystals in the anharmonic approximation

Janusz Tomaszewski, Cecylia Malinowska-Adamska, Piotr Słoma

Institute of Physics, Technical University of Łódź
Wólczańska 219, 93-005 Łódź, Poland

ABSTRACT

The reduced second-order approximation of the self-consistent phonon theory was applied some years ago for cubic metallic crystals whose interatomic interactions were approximated by the Morse and Lennard-Jones pair potential functions. Unfortunately, the parameters of these potentials were generally obtained with the help of semi-classical method basing on the classical static relationships between ground-state properties of a crystal and its interatomic potential, and the zero-point vibrations were taken into account only by certain corrections to the experimental data. Moreover, the further self-consistent calculations were being carried out semi-analytically which required some simplifications. In this paper we can reject them because all essential calculations are being carried out numerically. In the studies at high-temperature properties of selected fcc metallic crystals (Cu, Ag, Au) we take as a model of interatomic interactions the (α,m) Buckingham, (n,m) Lennard-Jones and (α,β) Morse pair potentials with the parameters determined self-consistently with the help of the experimental data for the zero-point lattice constant, cohesive energy and isothermal compressibility. Our new theoretical results for pressure variations of the limiting temperatures of dynamical and thermodynamical stability and for the stability criteria are collected and compared with available experimental data.

Keywords: self-consistent phonon theory, noble metals, stability of crystal lattices

1. INTRODUCTION

About 30 years ago Plakida and Siklós formulated[1] the self-consistent phonon theory (SCPT) using the double-time Green's functions method. The reduced second-order approximation of this theory (RSOSCPT) enables to study the dynamical and thermodynamical properties of the fcc crystal lattices with central interatomic interactions, with special regard to the high anharmonicity region, that is at high temperatures close to the melting point and also in the case of the so-called quantum crystals for which even the zero-temperature is too high to use the quasiharmonic treatment. In our previous papers we tried to describe self-consistently the physical properties of the rare gas solids (RGS) - both the heavier[2] and the lighter-quantum[3] ones. As a model of the interatomic interactions we used three pairwise potentials:

- (α,m) Buckingham (B)

$$\varphi_B(r)=\frac{\alpha\cdot m}{\alpha-m}\cdot D_0\cdot\left\{\frac{1}{\alpha}\cdot\exp\left[\alpha\cdot\left(1-\frac{r}{r_0}\right)\right]-\frac{1}{m}\cdot\left(\frac{r_0}{r}\right)^m\right\},\quad r\geq r_{extr}, \tag{1}$$

- (n,m) Lennard-Jones (LJ)

$$\varphi_{LJ}(r)=\frac{n\cdot m}{n-m}\cdot D_0\cdot\left[\frac{1}{n}\cdot\left(\frac{r_0}{r}\right)^n-\frac{1}{m}\cdot\left(\frac{r_0}{r}\right)^m\right],\quad n>m, \tag{2}$$

- (α,β) Morse (M)

$$\varphi_M(r)=\frac{\alpha\cdot\beta}{\alpha-\beta}\cdot D_0\cdot\left\{\frac{1}{\alpha}\cdot\exp\left[\alpha\cdot\left(1-\frac{r}{r_0}\right)\right]-\frac{1}{\beta}\cdot\exp\left[\beta\cdot\left(1-\frac{r}{r_0}\right)\right]\right\},\quad \alpha>\beta, \tag{3}$$

where n, m, α and β are the dimensionless parameters describing the slope of the potential curve, r_0 and D_0 define the potential minimum and are, respectively, the equilibrium distance of two isolated atoms and the energy of their dissociation.

Intl. Conference on Solid State Crystals 2000: Growth, Characterization, and Applications of Single Crystals, Antoni Rogaski, Krzysztof Adamiec, Pawel Madejczyk, Editors, Proceedings of SPIE Vol. 4412 (2001) © 2001 SPIE · 0277-786X/01/$15.00

In this paper we try to apply the RSOSCPT, in connection with the three mentioned potentials, to the noble metal crystals (NMC): copper, silver and gold. As for metals there is no simple expression like the r^{-6} law of attraction in the RGS, so we must use just these generalised 4-parameters versions of the traditional 2- or 3-parameters potentials: (α,6) Buckingham, (12,6) Lennard-Jones and (α,α/2) Morse.

The physical properties of the NMC were already being studied on the basis of the RSOSCPT in terms of the (α,α/2) Morse[4] and (n,m) Lennard-Jones[5] potentials but the potential parameters were obtained from the ground-state crystal properties with the help of the static relations[2,3] and so with neglect of the zero-point vibrations effect. In this paper we calculate the potential parameters self-consistently (dynamically) fitting them to the experimental data[6] for the zero-point cohesive energy, lattice constant and compressibility. Instead of the 4-th condition we assume correctness of the theoretical values of the parameter α in the repulsive Born-Mayer potential, evaluated by Hafemeister[7] with the help of the exchange charge model (ECM). It is also possible to take for α some of the experimental values reported by Hafemeister[7].

2. THE BASIS OF THE SELF-CONSISTENT CALCULATIONS

The self-consistent method of treating the lattice dynamics consists in replacing the pairwise static potential with its dynamical self-consistent version according to the following renormalization scheme:

$$\tilde{\varphi}(r) = \sum_{k=0}^{\infty} \frac{1}{k!} \cdot y^k \cdot r_0^{2k} \cdot \varphi^{(2k)}(r), \tag{4}$$

where $y = \overline{u^2} / 2r_0^2$ is the renormalization parameter,

$\overline{u^2}$ is the mean-square relative displacement of the neighbouring atoms, which depends on the temperature range and is always very complicated function of the self-consistent potential and its derivatives[1].

It is worth-while to point out here that, as it was shown by Plakida, Siklós and Aksienov[1,8], all the physical quantities connected with crystal lattice can be expressed as functions of $y(l)$, $\tilde{\varphi}(l)$, $\tilde{\varphi}''(l)$ and $\tilde{\varphi}'''(l)$, where l is the equilibrium interatomic separation derived from the equilibrium condition:

$$p = -(z \cdot l / 6 \cdot v) \cdot \tilde{\varphi}'(l), \tag{5}$$

where p is the external pressure, z and v are the number of nearest neighbours and the specific volume, respectively.

The self-consistent system of equations (4-5) possesses an implicit form with respect to the renormalization parameter and so it can be solved only approximately - for instance numerically. It is worth-while to point out here that the analysis of solvability of this system enables us to find the limiting temperature of the dynamical stability of crystal lattice - defined by Plakida and Siklós as the temperature at which the theoretical phonon frequencies become complex. From the other hand, the limiting temperature of the thermodynamical stability can be obtained with the help of the thermo-mechanical and elastic conditions derived from the principle of minimal free Gibbs energy. We don't go here into details because the problem of theoretical description of lattice stability was extensively discussed in our previous paper[9].

In the present study we make use of the self-consistent treatment in order to characterise the boundary of stability region of the NMC lattices.

3. NUMERICAL RESULTS AND CONCLUSIONS

Using the self-consistent relationships connecting the dynamical and thermodynamical quantities with the interatomic interaction function we have found the optimal values of the parameters n, m, α, β, r_0 and D_0 of the (α,m) Buckingham, (n,m) Lennard-Jones and (α,β) potentials for the NMC fitting them to the zero-point experimental data[6] for the nearest-neighbours mean separation l_0, the heat of sublimation L_0 and the isothermal bulk modulus B_0. We have decided to create for each crystal and potential two series of parameters. Namely, it is possible to take for the repulsive parameter α in the Buckingham and Morse potentials either the theoretical value (obtained by Hafemeister[7] with the help of the exchange charge model) or the experimental one (from among a few experimental values reported by Hafemeister[7] we choose every time the lowest one which differs the most from the ECM result). The mentioned zero-point experimental data and the results of calculations of the potential parameters (two series) are collected in Tables 1 and 2, respectively. Let us notice that the ratios n/m and α/β are always higher than 2. Additionally n and m differ distinctly from 12 and 6, respectively. D_0 and r_0 are almost the same for all the potentials.

Table 1. The experimental data[6] for the nearest-neighbours mean separation l_0, the heat of sublimation L_0 and the isothermal bulk modulus B_0 used in calculations of the pair potential parameters.

l_0 [10^{-10}m]			L_0 [10^{-21}J/atom]			B_0 [GPa]		
Cu	Ag	Au	Cu	Ag	Au	Cu	Ag	Au
2.549	2.876	2.875	561.4	471.9	611.6	133.3	100.0	166.7

Table 2. Optimal values of the parameters of the Buckingham (B), Lennard-Jones (LJ) and Morse (M) pair potentials for the noble metal crystals: copper, silver, gold. The two sets of parameters were obtained for $\alpha = \alpha_{theor}$ (*) and $\alpha = \alpha_{exp}$ (**).

Solid	Potential	n	m	α	β	r_0 [10^{-10}m]	D_0 [10^{-21} J]
Cu	B*	-	2.88	10.17	-	2.542	94.51
	B**	-	1.73	15.97	-	2.539	94.51
	LJ*	8.8	2.88	-	-	2.541	94.51
	LJ**	14.85	1.73	-	-	2.539	94.51
	M*	-	-	10.17	2.47	2.542	94.51
	M**	-	-	15.97	1.60	2.540	94.51
Ag	B*	-	3.19	11.53	-	2.870	79.3
	B**	-	2.05	17.07	-	2.869	79.3
	LJ*	10.15	3.19	-	-	2.870	79.3
	LJ**	16.0	2.05	-	-	2.868	79.3
	M*	-	-	11.53	2.8	2.870	79.3
	M**	-	-	17.07	1.91	2.869	79.3
Au	B*	-	4.18	11.49	-	2.872	102.5
	B**	-	2.62	17.09	-	2.871	102.5
	LJ*	9.93	4.18	-	-	2.871	102.5
	LJ**	15.9	2.62	-	-	2.871	102.5
	M*	-	-	11.49	3.6	2.872	102.5
	M**	-	-	17.09	2.43	2.871	102.5

Having at disposal the potential parameters we could carry out the analysis of solvability of the self-consistent system of equations (4-5) with respect to the renormalization parameter for different temperatures and pressures. As a result we have found for all the noble metal crystal lattices the pressure variations of the limiting temperature of the dynamical stability for the three models of interatomic interactions. The next step was to study the behaviour of the thermodynamical quantities within the dynamical stability region. We were especially interested in the high-temperature properties of the isothermal bulk modulus and the isothermal elastic constants c_{11}, $(c_{11} - c_{12})/2$ and c_{44}, which for the thermodynamically stable cubic structure should be positively defined. The temperature over which these conditions (at least one of them) are violated is in fact the limiting temperature of the thermodynamical stability. The results of calculations of the limiting temperatures of the dynamical and thermodynamical stability of crystal lattices of noble metals are collected in Table 3 together with the experimental data[10] for the melting temperature.

Table 3. Pressure variations of the limiting temperatures of the dynamical T_s^{dyn} and thermodynamical T_s^{tdm} stability of the noble metal crystals obtained in the RSOSCPT for the Buckingham, Lennard-Jones and Morse model potentials. Experimental values of the melting temperature T_m[10] are shown for comparison. All results in Kelvin scale

Cu	0 GPa		1 GPa		2 GPa		3 GPa		4 GPa	
	T_S^{dyn}	T_S^{tdm}	T_S^{dyn}	T_S^{tdm}	T_S^{dyn}	T_S^{tdm}	T_S^{dyn}	T_S^{tdm}	T_S^{dyn}	T_S^{tdm}
B*	3083	3077	3376	3345	3700	3614	4079	3886	-	4158
B**	1999	1920	2227	2088	2485	2256	-	2423	-	2589
LJ*	2626	2600	2826	2779	3030	2956	3237	3131	3448	3303
LJ**	1702	1633	1853	1755	2010	1875	2175	1992	-	2109
M*	3477	3469	3783	3750	4115	4031	4485	4314	-	4597
M**	2360	2218	2611	2391	2892	2562	-	2733	-	2902
T_m (Exp)	1356		1397		1435		1473		1501	

Ag	0 GPa		1 GPa		2 GPa		3 GPa		4 GPa	
	T_S^{dyn}	T_S^{tdm}	T_S^{dyn}	T_S^{tdm}	T_S^{dyn}	T_S^{tdm}	T_S^{dyn}	T_S^{tdm}	T_S^{dyn}	T_S^{tdm}
B*	2609	2603	2972	2931	3391	3263	-	3596	-	3931
B**	1807	1746	2105	1968	2466	2189	-	2410	-	2629
LJ*	2281	2259	2543	2493	2813	2723	3091	2949	-	3171
LJ**	1569	1511	1774	1676	1988	1838	-	1996	-	2153
M*	2917	2911	3294	3253	3717	3598	-	3943	-	4289
M**	2097	1994	2417	2222	2790	2447	-	2671	-	2894
T_m (Exp)	1234		1288		1353		1401		1485	

Au	0 GPa		1 GPa		2 GPa		3 GPa		4 GPa	
	T_S^{dyn}	T_S^{tdm}	T_S^{dyn}	T_S^{tdm}	T_S^{dyn}	T_S^{tdm}	T_S^{dyn}	T_S^{tdm}	T_S^{dyn}	T_S^{tdm}
B*	3742	3742	4061	4053	4402	4368	4773	4685	5196	5006
B**	2687	2632	2954	2850	3243	3068	3563	3286	-	3504
LJ*	3341	3327	3594	3561	3852	3793	4116	4024	4387	4253
LJ**	2386	2322	2584	2489	2787	2654	2995	2818	3210	2979
M*	4079	4079	4406	4401	4752	4727	5124	5055	5530	5386
M**	3045	2959	3327	3183	3629	3407	3958	3630	4333	3853
T_m (Exp)	1338		1393		1447		1502		1562	

As we see, the thermodynamical stability conditions nearly always prevail over the dynamical ones - especially for high pressures and harder potentials (like the (n,m) Lennard-Jones). Moreover, the RSOSCPT provides a disappearance of the dynamical instability (but not the thermodynamical one) at sufficiently high pressures - the external forces become then strong enough to localise atomic vibrations for any given temperature. Consistently with the expectations both T_s^{dyn} and T_s^{tdm} are always greater then the real melting temperature T_m and the difference is the lowest in the case of the (n,m) Lennard-Jones (LJ**) potential with the attraction parameter m taken from the ($\alpha=\alpha_{ECM}$, m) Buckingham potential.

Within the investigations of the destabilisation phenomenon in the NMC we have studied the pressure variations of the ratio $\kappa=\left(\overline{u^2}\right)^{1/2}/l$, of the mean amplitude of relative thermal vibrations of neighbouring atoms to the equilibrium interatomic spacing, calculated at the limit of stability (κ_S^{dyn}, κ_S^{tdm}) (Table 4).

Table 4. Pressure variations of the dynamical and thermodynamical stability criteria of the noble metal crystals obtained in the RSOSCPT for the Buckingham, Lennard-Jones and Morse model potentials. The meaning of symbols is as in Table 2.

Cu	0 GPa		1 GPa		2 GPa		3 GPa		4 GPa	
	κ_S^{dyn}	κ_S^{tdm}	κ_S^{dyn}	κ_S^{tdm}	κ_S^{dyn}	κ_S^{tdm}	κ_S^{dyn}	κ_S^{tdm}	κ_S^{dyn}	κ_S^{tdm}
B*	0.1467	0.1441	0.1538	0.1461	0.1628	0.1476	0.1775	0.1492	-	0.1506
B**	0.1250	0.1093	0.1314	0.1103	0.1413	0.1112	-	0.1121	-	0.1128
LJ*	0.1286	0.1224	0.1312	0.1230	0.1346	0.1236	0.1376	0.1242	0.1406	0.1247
LJ**	0.1070	0.0949	0.1097	0.0953	0.1143	0.0957	0.1206	0.0959	-	0.0962
M*	0.1529	0.1497	0.1589	0.1516	0.1658	0.1530	0.1751	0.1545	-	0.1558
M**	0.1326	0.1132	0.1384	0.1141	0.1473	0.1148	-	0.1155	-	0.1162

Ag	0 GPa		1 GPa		2 GPa		3 GPa		4 GPa	
	κ_S^{dyn}	κ_S^{tdm}	κ_S^{dyn}	κ_S^{tdm}	κ_S^{dyn}	κ_S^{tdm}	κ_S^{dyn}	κ_S^{tdm}	κ_S^{dyn}	κ_S^{tdm}
B*	0.1332	0.1300	0.1423	0.1324	0.1547	0.1345	-	0.1363	-	0.1379
B**	0.1150	0.1024	0.1254	0.1037	0.1461	0.1049	-	0.1060	-	0.1069
LJ*	0.1181	0.1126	0.1222	0.1136	0.1268	0.1144	0.1313	0.1151	-	0.1157
LJ**	0.1002	0.0897	0.1050	0.0903	0.1104	0.0908	-	0.0911	-	0.0915
M*	0.1373	0.1348	0.1456	0.1370	0.1557	0.1390	-	0.1406	-	0.1422
M**	0.1218	0.1058	0.1305	0.1070	0.1429	0.1080	-	0.1089	-	0.1097

Au	0 GPa		1 GPa		2 GPa		3 GPa		4 GPa	
	κ_S^{dyn}	κ_S^{tdm}	κ_S^{dyn}	κ_S^{tdm}	κ_S^{dyn}	κ_S^{tdm}	κ_S^{dyn}	κ_S^{tdm}	κ_S^{dyn}	κ_S^{tdm}
B*	0.1240	0.1240	0.1297	0.1267	0.1354	0.1283	0.1421	0.1296	0.1538	0.1309
B**	0.1094	0.1001	0.1149	0.1010	0.1219	0.1019	0.1296	0.1027	-	0.1034
LJ*	0.1135	0.1099	0.1167	0.1106	0.1191	0.1112	0.1218	0.1119	0.1255	0.1125
LJ**	0.0979	0.0887	0.1001	0.0891	0.1029	0.0895	0.1058	0.0898	0.1095	0.0901
M*	0.1278	0.1278	0.1329	0.1306	0.1374	0.1321	0.1436	0.1334	0.1512	0.1346
M**	0.1146	0.1033	0.1194	0.1041	0.1248	0.1049	0.1316	0.1056	0.1435	0.1063

As it appears the thermodynamical stability criterion κ_S^{tdm} is nearly independent of pressure if crystal and the model potential are fixed while the dynamical stability criterion κ_S^{dyn} rises rapidly with pressure in all cases. The last fact means that the dynamical destabilisation becomes more and more difficult when the external pressure increases and so at higher pressures the melting phenomenon is rather caused by the order-disorder transition.

4. CONCLUSIONS

Summarising, we would like to stress, that the RSOSCPT provides a disintegration of the noble metal crystal lattices as an effect of extreme thermal vibrations of lattice atoms. The theoretical limiting temperatures of the dynamical and thermodynamical stability are always the upper estimations of the real melting temperature. The quality of this estimation is generally better in the case of the thermodynamical treatment and harder potential functions. If it about the two series of potential parameters, the results obtained with the help of parameters α and m derived from experiment are better than in the case of the parameters obtained purely theoretically with the help of the exchange charge model. It is worth-while to point out here that there exists no theoretical prediction for the value of T_S - T_m , and the only proper method of determining the melting temperature is the method based on the analysis of the equation of state and the thermodynamical potentials simultaneously for solid and liquid. Anyway, we must be aware of the fact that the reduced second-order approximation of the SCPT is formulated only for central, nearest-neighbours interactions and so it should be improved. In addition the real interactions in the metallic crystals are in significant part non-central and so we should rather evaluate the repulsive parameter α using the additional experimental data and if we want to describe the interactions theoretically a many-body, non-central force must be considered.

REFERENCES

1. N.M. Plakida, T. Siklós, "Theory of anharmonic crystals", *Phys. Stat. Sol.* **33**, pp. 103-112 and 113-123, 1969; **39**, pp. 171-180, 1970.
2. C. Malinowska-Adamska, P. Słoma, J. Tomaszewski, "Self-consistent calculations of the thermodynamic and elastic properties of heavier rare gas solids near the lattice instability point", *Phys. Stat. Sol.* **(b)219**, pp. 229-240, 2000.
3. C. Malinowska-Adamska, P. Słoma, J. Tomaszewski, "Application of the Lennard-Jones (n,m) potential function to quantum crystals in the self-consistent phonon theory", *Phys. Stat. Sol.* **(b)200**, pp. 451-462, 1997.
4. C. Malinowska-Adamska, "Self-consistent calculations of the lattice dynamics and thermodynamics of anharmonic noble metals", *Phys. Stat. Sol.* **(b)120**, pp. 601-610, 1983.
5. C. Malinowska-Adamska, "The effect of pressure on the thermodynamic properties of crystals near the lattice instability point", *Phys. Stat. Sol.* **(b)151**, pp. 53-60, 1989.
6. Shu Zhen, G.J. Davies, "Calculation of the Lennard-Jones n-m potential energy parameters for metals", *Phys. Stat. Sol.* **(a)78**, pp. 595-605, 1983.
7. D.W. Hafemeister, "Calculation of the ion-ion repulsive interaction in the rare gas solids and in the noble metals", *J. Phys. Chem. Solids* **30**, pp. 117-128, 1969.
8. N.M. Plakida, V.L. Aksienov, "Elastic constants and stability of anharmonic crystals", *Solid State Physics* **15**, pp. 2575- 2582, 1973 (in Russian).
9. J. Tomaszewski, C. Malinowska-Adamska, "Self-consistent description of the lattice destabilisation phenomenon for the heavier rare gas solids", *Proc. SPIE* **3724** , pp. 177-182, 1999.
10. L.H. Cohen, W. Klement, Jr., G.C. Kennedy, "Melting of copper, silver and gold at high pressures", *Phys. Rev.* **145**, pp. 519-525, 1966.