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INVESTIGATION OF ELASTIC CONSTANTS AND MODULI OF BINARY ALLOYS BY STATISTICAL MOMENT METHOD

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ABSTRACT

The moment method in statistical dynamics is used to study the dynamical elastic constants (C_{11}, C_{12}, C_{44}), Young's modulus (E), bulk modulus (K), and shear modulus (G) of binary alloys. Lattice mechanical properties of disorder alloys are calculated as a function of the temperature. In most cases there is a good agreement between the present and the experiment.

KEYWORDS: Lattice mechanical properties, elastic constants, elastic moduli, binary alloys, statistical moment method

1. Introduction

Elastic deformation is one of the most important considerations in structural applications of solid materials. In recent years, there has been considerable interest in elastic-plastic deformation of materials. Some of these studies are listed in Refs. 1 and 2.

Various theoretical studies have been used to study the dynamical elastic properties of simple metals and alloys. Phonon spectrum and lattice mechanical properties of metals have been calculated using *ab-initio* theory [2, 3]. Recently, a pseudo potential model depending on the effective core radius is used to study the interatomic interactions, dynamical elastic constants (C_{11}, C_{12}, C_{44}) and Young's modulus (E), the behavior of phonon frequencies, etc., for simple metals and alloys [4]. Rare-earth and actinide elements such as La, Yb, Ce, Th... also have been considered by the same method [5].

In this paper we have calculated dynamical elastic constants (C_{11}, C_{12}, C_{44}), Young's modulus (E), bulk modulus (K), and shear modulus (G) by using the statistical moment method (SMM) [6,7]. In Sec. 2, the analytic expressions for elastic moduli (E, K, G) and dynamical elastic constants are given. In Sec. 3, the SMM calculations are performed by using effective pair potentials for Cu-Zn, Cu-Ni, Ni-Cr, Al-Cu, Al-Mg, Pd-Ag…alloys with various concentrations and compared to the experimental results.

2. Theory

2.1. Free energy and the nearest neighbor distance of binary alloy

We consider a binary alloy consisting of two components A and B neglecting vacancies and interstitials with face-centered cubic structure (f.c.c) and body-centered cubic structure (b.c.c). C_A, C_B are the concentration of atoms A, B, respectively. The atoms chosen as base are atom α located in lattice point β. This system is called effective systems (α, β). The free energy of the system may be determined by the combination of the free energy of these effective system (α, β) as:

$$\Psi = \left(\upsilon_a p_A^a \Psi_A^a + \upsilon_b p_A^b \Psi_A^b + \upsilon_a p_B^a \Psi_B^a + \upsilon_b p_B^b \Psi_B^b\right) - TS_c = \sum_{\alpha,\beta} \upsilon_\beta p_\alpha^\beta \Psi_\alpha^\beta - TS_c, \quad (1)$$

where υ_a, υ_b the concentration of the lattice points of type a, b. p_α^a, p_α^b (α = A, B) are the probability of atom α located in the lattice points a, b, respectively. Probabilities p_α^β (β = a, b) satisfy the following relations:

$$p_A^a + p_B^a = 1;\ p_A^b + p_B^b = 1;\ \upsilon_a p_A^a + \upsilon_b p_A^b = C_A;$$

$$\upsilon_a p_B^a + \upsilon_b p_B^b = C_B;$$

Ψ_α^β is the free energy of the effective system (α, β) and S_c is the entropy of mixing.

$$S_c = k \ln\left[\frac{(N_A + N_B)!}{N_A! N_B!}\right] \quad (2)$$

with: k is the Boltzmann constant.

In order to define Ψ_α^β we use the statistical moment method (SMM) described in [6, 7]. The free energy of the effective system (α, β) will have the form of the free energy of the systems of N harmonic oscillator [7]

$$\Psi_\alpha^\beta = 3N\left\{\frac{u_{o\alpha}^\beta}{6} + \theta\left[x_\alpha^\beta + \ln(1 - e^{-2x_\alpha^\beta})\right]\right\} \quad (3)$$

with:

$$x_\alpha^\beta = \frac{\hbar\omega_\alpha^\beta}{2\theta} = \frac{\hbar}{2\theta}\sqrt{k_\alpha^\beta / m^*}, \quad (4)$$

where: $m^* = C_A m_A + C_B m_B$; m_A, m_B are the mass of atoms A and B, and the sum of the effective pair interaction energies of the effective system (α, β), $u_{o\alpha}^\beta$, and the second - order vibrational constant, k_α^β, are given as:

$$u_{o\alpha}^\beta = \sum_i \varphi_{\alpha i}^\beta\left(|a_i|\right)$$

$$k_\alpha^\beta = \frac{1}{2}\sum_i\left(\frac{\partial^2\varphi_{\alpha i}^\beta}{\partial u_{ix}^2}\right)_{eq} \equiv m^*\left(\omega_\alpha^\beta\right)^2; \quad (5)$$

here: $\varphi_{\alpha i}^\beta(|a_i|)$ is the potential energy of interaction between particle i-th and the base particle, a_i is the vector determining the equilibrium position of particle i, u_i the displacement of i-th particle from its equilibrium position.

In the case of disorder alloys AB, we have [6]:

$$\Psi_A^a = \Psi_A^b = \Psi_A^*, \quad \Psi_B^a = \Psi_B^b = \Psi_B^*, \quad (6)$$

where: Ψ_α^* / N is the free energy of atom α (α,α'=A,B) surrounded by $J_{1\alpha} = n_1 p_{\alpha\alpha'} / C_\alpha$ of atoms α' and (n_1 - $J_{1\alpha}$) of atoms α on the first coordination sphere and $J_{2\alpha} = n_2 p_{\alpha'}^\beta = n_2 C_{\alpha'}$ of atoms α' (and (n_2 - $J_{2\alpha}$) of atoms α on the second coordination sphere; n_1, n_2 is the number of the atoms on the first and second spheres.

Then, we can find the expression of the free energy of disorder alloy with $C_B << C_A$:

$$\Psi_{AB} \approx C_A\Psi_A + C_B\Psi_B - TS_c, \quad (7)$$

where: ψ_α is the free energy of the effective metal α.

In order to define the nearest neighbor distance, we can use some different ways. In this paper, the nearest neighbor distance is determined by minimizing the free energy with respect to the volume of the system and we obtain the expression of the nearest neighbor distance of disorder binary alloy [8]:

$$a \cong C_A a_A \frac{B_{T,A}}{\overline{B_T}} + C_B a_B \frac{B_{T,B}}{\overline{B_T}} \quad (8)$$

where:

$$\overline{B_T} = C_A B_{T,A} + C_B B_{T,B},$$

$$B_{T,\alpha} = \left(\frac{\partial^2\Psi_\alpha}{\partial a_\alpha^2}\right)_{T,p,N} = \frac{1}{2}\left(\frac{\partial^2 u_{o\alpha}}{\partial a_\alpha^2}\right)_{T,p,N} + \frac{3\hbar\omega_\alpha}{4k_\alpha}\left[\left(\frac{\partial^2 k_\alpha}{\partial a^2}\right)_{T,p,N} - \frac{1}{2k_\alpha}\left(\frac{\partial k_\alpha}{\partial a}\right)^2_{T,p,N}\right], \quad (9)$$

with: a_α is the nearest neighbor distance at temperature T of the effective metal α.

2.2. Dynamical elastic constants and moduli

If Ψ_{AB} is the Helmholtz free energy for a volume element of the considered system in the case without external force p, Ψ_{AB}^P is the one in the case of external force P, ε is the elastic strain, σ is the stress, the relation of these quantities can be written in the approximation form [9]:

$$\Psi_{AB}^P = \Psi_{AB} + \frac{E\,\varepsilon^2}{2}. \quad (10)$$

In the above expression, the term $\frac{E\,\varepsilon^2}{2}$ is the deformation energy for a volume element of the system, E is the Young's modulus.

From the definition of the elastic strain ε, we have:

$$\varepsilon = \frac{\Delta a_{AB}}{a_{AB}} = \frac{a^P_{AB} - a_{AB}}{a_{AB}} \qquad (11)$$

here: a_{AB}, a^P_{AB} is the nearest neighbor distance of the system in the case without and with external force P, respectively, and has the form

$$a_{AB} = a_{0AB} + y_0\,,\ a^P_{AB} = a^P_{0AB} + y\,, \qquad (12)$$

where: a_{0AB} and a^P_{0AB} is the nearest neighbor distance of the system in the case without external force P and in the case of external force P at zero temperature, respectively; y is the displacement of atom in the case of external force P [7]

$$y = y_0 + A_{1AB}\,P + A_{2AB}\,P^2 \qquad (13)$$

here: y_0 is the displacement of atom in the case without external force P.

In the case of elastic deformation, when $\Delta a_{0AB} = a^P_{0AB} - a_{0AB} \approx 0$, from Eq. (11), (12) and (13), we have:

$$\varepsilon \approx \frac{y - y_0}{a_{AB}} \approx \frac{y_0 + A_{1AB}P - y_0}{a_{AB}} = \frac{A_{1AB}P}{a_{AB}}. \qquad (14)$$

Using the relation of the stress σ and the strain ε for the Hookean deformation, so we have $\frac{\partial\sigma}{\partial\varepsilon} = E$, and Eqs. (10) and (14), we obtain the expression of the Young's modulus E:

$$E = \frac{\sigma a_{AB}}{A_{1AB}P} = \frac{1}{\pi a_{AB}A_{1AB}}\ . \qquad (15)$$

Because a_{AB} and A_{1AB} depend on temperature [8], so Eq. (15) is the expression of the Young's modulus at various temperatures.

Using the relation of the Young's modulus E with bulk modulus K and shear modulus G [10], we obtain the analytic expressions for elastic moduli:

$$K \approx \frac{E}{3(1-2\upsilon)}\ ,\quad G = \frac{E}{2(1+\upsilon)} \qquad (16)$$

with υ is the Poisson's ratio.

It is known that for cubic crystals, the elastic constants are [11]

$$C_{11} = \frac{E(1-\upsilon)}{(1+\upsilon)(1-2\upsilon)}\ ,$$
$$C_{12} = \frac{E\upsilon}{(1+\upsilon)(1-2\upsilon)},\ C_{44} = \frac{E}{2(1+\upsilon)}. \qquad (17)$$

3. Results and discussion

In order to check the validity of the analytical expressions of the elastic properties of the metallic systems described herein, we performed calculations for some disorder binary alloys. For simplicity, we take the effective pair interaction potential in the systems as the power law, similar to the Lennard-Jones pair interaction potential:

$$\varphi(r) = \frac{D}{n-m}\left[m\left(\frac{r_0}{r}\right)^n - n\left(\frac{r_0}{r}\right)^m\right], \qquad (18)$$

where the potential parameters such as D and r_0 are determined to fit experimental data (e.g., cohesive energy and elastic modulus). Using the experimental data of the potential parameters D, r_0 and the Poisson's ratio υ (Tab. 1) and the expressions obtained in Sec. 2, we calculated the values of the elastic constants and moduli at temperature T and the zero pressure for Cu-Zn, Cu-Ni, Al-Cu,… alloys with various concentrations. The calculated results are presented in Tabs. 2-5.

In Tab. 2, we show the calculated values of the nearest neighbor distance a_{AB} of Fe_xCu_{1-x} alloys at 0K. In Tabs.3 and 4, we show our calculated and experimental results of the elastic moduli at various temperatures. The accuracy of the elastic moduli is remarkably good. The elastic moduli of Pd-80Ag (at T=293K) and Al-4.5Cu (at T=300K) alloys are in excellent agreement with the experimental results.

Using Eqs. (17), we calculate the values of the elastic constants at temperature T and zero pressure for Ag-Mg, Ag-Pd, Cu-Zn, … alloys. Our calculated and experimental results of C_{11} at 300K are presented in Tab. 5. The present SMM calculations of the elastic constants agree well with the experimental values. All of the case are in excellent agreement with the experimental results, within ~0.9% for Ag-7.33Mg, Cu-4.59 Zn,… alloys.

The decrease of the elastic moduli and constants with increasing temperature arises from the thermal lattice expansion and the inharmonic effects of the vibrational. These results are presented in Fig. 1 and Fig. 2. The SMM calculations are performed by using the effective pair potential for Cu-Zn, Cu-Ni, Ni-Cr, Al-Cu, Al-Mg, Pd-Ag… alloys. In general, we have obtained good agreement in the elastic constants and moduli between our theoretical calculations and experimental values.

Tab.1. *Potential parameters D, r_o, m, n and the Poisson's ratio υ determined by the experiment [12]*

Metals	m	n	r_0 (A^o)	D (10^{-16} erg)	υ
Ag	5.5	11.5	2.8760	4589.328	0.38
Al	5.5	11.0	2.8541	4133.928	0.34
Ni	8.0	9.0	2.4780	5971.536	0.30
Cu	5.5	11.0	2.5487	4693.518	0.37
Pt	5.0	9.2	2.7689	9914.196	0.40
Pd	5.0	9.0	2.7432	7559.778	0.38
Ir	5.0	11.0	2.8847	11750.148	0.26
Fe	7.0	11.5	2.4775	6416.448	0.26
Mg	4.5	14.0	3.1882	2069.034	0.30
Zn	5.5	10.0	2.7622	2320.47	0.35
Cr	6.0	15.5	2.4950	6612.960	0.33

Tab.2. *SMM calculations of the nearest neighbor distance a_{AB} of Fe_xCu_{1-x} alloys at 0K and ab-initio results [13]*

		Fe-10.0Cu	Fe-25.0Cu	Cu-25.0Fe
$a_{AB}(A^0)$	SMM	2.404	2.410	2.458
	ab-initio	2.494	2.494	2.490

Tab.3. *SMM calculations and Expt. results of Young's modulus E (in 10^{10} Pa) at T=586K for alloys*

Alloys	Cu-5.0Zn	Cu-10.0Zn	Cu-20.0Zn	Cu-30.0Ni	Ni-20.0Cr
SMM	11.11	10.71	9.92	13.81	20.00
Expt. [14]	11.70	11.70	11.00	15.20	21.00

Tab.4. *SMM calculations and Expt. results of Young's modulus E (in 10^{10} Pa) at T=293K, T=300K for alloys (Expt.^{a} [12]; Expt.^{b} [14])*

		T= 293^{0}K		T=300^{0}K			
	Alloys	Pd-80.0Ag	Pt-10.0Ir	Al-4.5Cu	Al-3.8Mg	Al-8.0Mg	Al-10.0Mg
E	SMM	9.0	16.6	7.26	6.82	6.59	6.48
	Expt.	9.0^a	15.0^a	7.10^b	7.10^b	7.10^b	7.10^b
G	SMM			2.67	2.51	2.42	2.38
	Expt.			2.65^b	2.65^b	2.65^b	2.65^b

Tab.5. *SMM calculations and Expt. results of elastic constant C_{11} (in 10^{11} Pa) at T=300K for alloys (Expt. [14])*

Alloys	Ag-3.07Mg	Ag-7.33Mg	Ag-6.22Pd	Ag-2.4Zn	Ag-3.53Zn
SMM	1.209	1.162	1.296	1.222	1.211
Expt.	1.198	1.159	1.277	1.209	1.230
Alloys	Cu-4.1Zn	Cu-4.59Zn	Cu-9.1Zn	Cu-17.1Zn	Cu-4.81Al
SMM	1.651	1.644	1.587	1.482	1.678
Expt.	1.633	1.634	1.571	1.499	1.658

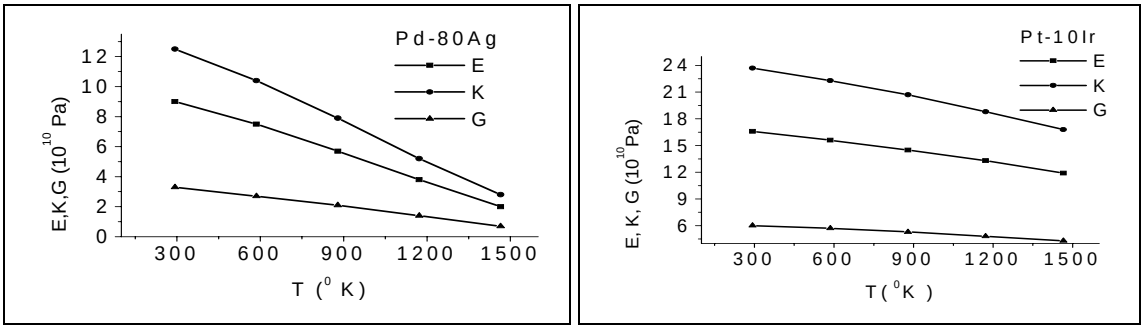

Fig. 1. *The dependence of the Elastic moduli on the temperatures for Pd-80Ag and Pt-10Ir alloys*

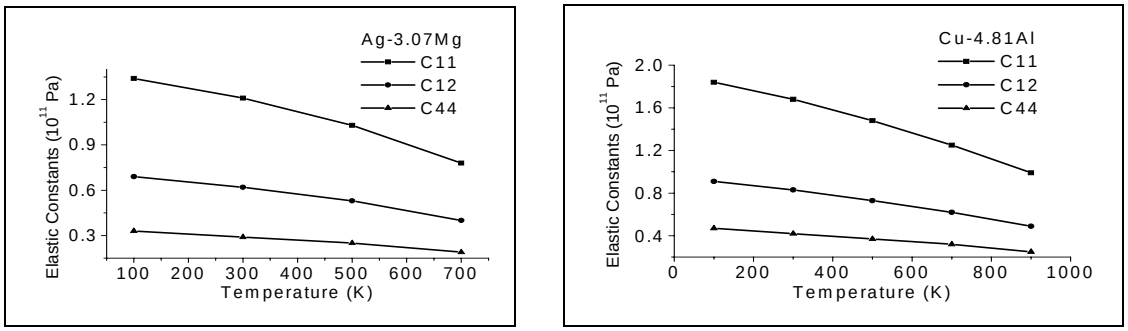

Fig. 2. *The dependence of the Elastic constants on the temperatures for Ag-3.07Mg and Cu-4.81Al alloys*

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