

ENTROPY OF METALS BASED ON THE THEORY OF FREE ELECTRON APPROXIMATION USING THERMODYNAMIC POTENTIALS

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Abstract

Generalized equation for computing entropy of metals was derived based on theory of free electron approximation using the knowledge of thermodynamic potentials. Poisson ratio representing the negative ratio of transverse and longitudinal strains is taking into consideration during computation. There is agreement between computed and theoretically obtained experimental value. The experimental results used in this work is theoretically obtained by substituting directly the experimental value of fermi energy (6) into the model used for computation using the mathematical relation between the fermi energy and electron density parameter. Entropy of metals depend on electronic concentration, average electron distance and statistical structure factor. As temperature increases entropy of metals increases due to increase in kinetic energy between interacting electron. Also, increase in entropy as temperature and strain rises is due to atomic disorder and displacement of atoms from their regular atomic site. Entropy of Potassium is the highest during deformation while Tungsten has the lowest entropy during deformation as a result of variation in their atomic tensile strength.

Keywords: Entropy, strain/deformation, free electron approximation, thermodynamic potential.

1.0 Introduction

Structure of solid is determined by balance of attractive and repulsive forces acting between its atoms [1]. Cohesion of solids results essentially from attractive electrostatic interaction between negative charge of valence electrons and positive charge of atomic nuclei [2]. Developments in the field of quantum theory of solids opened vast opportunities for better understanding and utilization of various materials [1]. Many fundamental properties of metals, e.g. electrical and thermal conductivities, magnetic and optical properties, etc. depend on their electronic structure [3]. Many physical properties of metals are understood in terms of electron theory of metals. The development of electron theory of metals forms the basis for classification of metals [4]. When free electron theory is applied to metals, it explains forces of cohesion and repulsion, binding of energy levels, behaviour of conductors and insulators and their magnetic properties [5]. In free electron theory, valence electrons of the constituent atoms become conduction electrons and move about freely throughout the volume of metal [1]. Deformation exists in solid when stress is applied. For small deformation, all solids behave in elastic manner. This linearity in elastic response is a direct consequence of limiting harmonic form for interatomic potential for small strain. For higher strains, Hooke's law may break down because the potential is no longer harmonic due to likely structural defects (e.g. dislocations) which facilitates plastic (i.e. permanent) deformation under an applied stress [2]. In metal, valence electrons are free to move in different directions, this valence electrons are called free electrons and are constrained only by metal surface [5]. The behaviour of free electrons moving in metals is considered to be similar to that of atoms or molecules in a perfect gas. Free electrons are referred to as free electron gas and movement of electrons obeys classical laws of kinetic theory [1]. Traditionally, Physicists treat electrons in crystals as a delocalized wave extending throughout the solid [6]. The allowed wave-like solutions of quantum-mechanical Schrodinger equation for electrons moving in an appropriate potential is labelled according to wavevectors of waves resulting in a concise description of allowed electron states as bands of allowed energies in reciprocal space in exact analogy with dispersion curves of phonons in crystals. This reciprocal-space

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description gives a very powerful approach which allows electronic properties to be calculated relatively straightforwardly by employing simplifying features of symmetry [2]. Entropy provides a computational method of encoding the intuitive notion of which processes are impossible even though they do not violate the fundamental law of conservation of energy [7]. Entropy is one of the most important concepts in physics, information theory and a measure of thermal energy of system per unit temperature [8]. Entropy provides a reliable insight into direction of spontaneous change for many everyday phenomena [9]. Entropy relates macroscopic and microscopic aspects of nature and determines the behaviour of macroscopic system [10]. Application of thermodynamics to study of crystals offers a powerful quantitative tool for investigating important properties of solid [6]. Clausius introduced the concept of entropy as a precise way of expressing the second law of thermodynamics to provide a quantitative measure for direction of spontaneous change. Clausius form of second law states that, the most probable process that may occur in an isolated system are those whose entropy either increase or remain constant [11]. That is, $S = k \ln \Omega$ where S is entropy, Ω represent the maximum number of microscopic ways in which the macroscopic state corresponding to entropy S can be realized and k is Boltzmann constant. A lot of experimental and theoretical model have been developed and used to studied some properties of metals. Tekuchev, et. al. [12], studied the entropies of iron, cobalt, rhodium, and platinum based on acoustic data using Debye theory and rigid-sphere model at different boiling point. A formula for melting entropy of metals is validated. There is good agreement between the results obtained and other literature data. Fang et. al. [13] developed a thermodynamic entropy model of cutting fluid based on thermodynamic theory. The internal mechanism of entropy generation in cutting fluid was demonstrated using external entropy flow and internal entropy generation. The dynamic entropy equilibrium equation of metal cutting system which provide an effective way of selecting cutting fluid is obtained. Muhammad, et. al. [14], demonstrated the interaction of rich variety of deformation mechanisms in high-entropy alloys with dislocation slip, stacking faults and twinning before transitioning to inhomogeneous deformation by serrations using in situ neutron diffraction. Result obtained shows that high-entropy alloys exhibit exceptional mechanical properties at cryogenic temperature due to activation of twinning in addition to dislocation slip. Coexistence of multiple deformation pathways shows how deformation mechanisms synergize during plastic deformation. Low stacking fault energy plus stable face-centred cubic structure at ultralow temperatures enabled by high-entropy alloying played a pivotal role in bridging dislocation slip and serration. Insights from in-situ experiments point to the role of entropy in the design of structural materials with superior properties. In this report, a theoretical model for computing entropy of metals is developed based on theory of free electron approximation using the knowledge of thermodynamic potential and used to study how entropy of metals varies with electron density parameter, temperature and linear deformation/strain. Adesakin, et. al. [15], developed a theoretical model for computing magnetic moment of metals based on free electron theory. Factors connecting compression to elongation during strain in metals is involved in the computation. Result obtained agree quite well with experimental value which shows that free electron theory is useful for theoretical prediction of some properties of metals. Magnetic moment of metals depends on spin and orbital configuration. Magnetic field influence magnetic moment of metals due to rotation of magnetic dipole and that magnetic field in metals is weakened by induced magnetization. Magnetic moment of metals subjected to deformation decreases as strain increases. Magnetic moment of all metals computed is negative, this is due to spin intrinsic properties and negative electric charge possess by electrons in metal. In this report, entropy of metals was examined based on the theory of free electron approximation using the knowledge of thermodynamic potentials. The metals were selected from different groups and periods. Thakor et.al. [16] investigated the internal energy, entropy and Helmholtz free energy of liquid alkali metals using pseudopotential perturbation scheme based on Gibbs-Bogoliubov variational technique. A local pseudopotential was used to describe the electron-ion interaction in the liquid alkali metals. They introduced the exchange and correlation effects, by employing the local field correction function proposed by Taylor. The results of the computed values for internal energy, entropy and Helmholtz free energy for the liquid alkali metals are in excellent agreement with the experimental data. Baria and Jani [17] used their recently proposed model potential to calculate enthalpy, entropy and Helmholtz free energy of liquid transition and rare earth metals with the variational approach. They determined the parameter of the potential with the standard zero pressure condition along with well-established Sarkar et al screening function for exchange and correlation effect. They strongly emphasize that the parameter of the potential is independent of any fitting procedure either with any experimental data or with any theoretical values of any physical properties. They employed the structure factor derived by Percus-Yevick solution for hard sphere fluids, which is characterized by hard sphere diameter. A good agreement between theoretical investigations and experimental findings has confirmed the ability of the model potential to the liquid d and f – shell metals. Michael and Michael [18] based on the information required to specify a liquid structure equals, which in suitable units, its thermodynamic entropy. Hence, they employed an expansion of the entropy in terms of multi-particle correlation functions which can be interpreted as a hierarchy of information measures. They utilized the first principles molecular dynamics simulations, to simulate the structure of liquid aluminum and obtained its density, pair and triplet correlation functions, allowing them to approximate the experimentally measured entropy and relate the excess entropy to the information content of the correlation functions.

They were able to discuss the accuracy and convergence of the method and found out that the entropy of liquid aluminum is described rather accurately using the first two terms in an expansion of the entropy in multiparticle correlation.

2.0 Theory and Calculation

The lattice heat capacity for free electron is expressed as

$$c_v = \left(\frac{\partial U}{\partial T}\right)_v = \int_0^{\omega_{max}} k_B \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{\exp(\hbar\omega/k_B T)}{(\exp(\hbar\omega/k_B T)-1)^2} N(\omega) d\omega \tag{1}$$

The solution to equation (1) is

$$c_v = \left(\frac{\partial U}{\partial T}\right)_v = \frac{\pi^2}{2} N K_B \left(\frac{T}{T_F}\right) \tag{2}$$

where the frequency distribution function for linear monatomic lattice with a cut-off frequency ω_{max} is

$$N(\omega) = \frac{2N/\pi}{(\omega_{max}^2 - \omega^2)^{1/2}} \tag{3}$$

The entropy of the free electron gas is obtained using the relation

$$\left(\frac{\partial U}{\partial T}\right)_v = T \left(\frac{\partial S}{\partial T}\right)_v \tag{4}$$

From the relation in equation (4) the entropy of free electron gas is

$$dS = \frac{1}{T} \left(\frac{\partial U}{\partial T}\right) dT \tag{5}$$

where

$$C_V = \left(\frac{\partial U}{\partial T}\right) \tag{6}$$

Hence, equation (5) becomes

$$S = \int_0^T \frac{C_V}{T} dT \tag{7}$$

Substituting the electronic heat capacity in equation (2) into equation (7), the entropy of the free electron gas become

$$S = \int_0^T \frac{1}{T} \frac{\pi^2}{2} N k_B \left(\frac{T}{T_F}\right) dT \tag{8}$$

Solving equation (8), entropy of free electron gas is obtained as

$$S = \frac{\pi^2}{2} N K_B \left(\frac{T}{T_F}\right) \tag{9}$$

Where N is the number of electrons, k_B is Boltzmann constant, T is temperature and T_F is Fermi temperature obtained as

$$T_F = \frac{\hbar}{2m_e k_B} (3\pi^2 n)^{\frac{2}{3}} \tag{10}$$

where n is the average electron density, \hbar is normalized Planck's constant and m_e is electron mass.

Putting equation (10) into equation (9), entropy of free electron gas becomes,

$$S = \frac{\pi^2}{2} N K_B \left(\frac{2m_e k_B T}{\hbar T_F (3\pi^2 n)^{\frac{2}{3}}}\right) \tag{11}$$

In this report, entropy of metals was computed and studied using equation (11). How linear strain affect entropy of metals is investigated. The metals were selected from different groups and periods based on the Poisson's ratio which is the physical constant required for the computation. The Poisson's ratio determines the ratio of transversal compression to elongation in the direction of applied deformation, uniaxial strain that express the extent to which the metal is deformed.

3.0 Results and Discussion

Figure 1 shows variation of entropy with electron density parameter for metals from different groups and periods. In figure 1, there is good agreement between computed and theoretically obtained experimental value for entropy of metals, this shows that free electron approximation theory is useful in theoretical predictions of entropy of metals as it takes into consideration some of the parameters that is required in computing entropy of metals. Figure 1 revealed that entropy of metals increases as electron density parameter increases. Metals whose entropy were computed concentrated more in the region of high-density limit than low density limit. These suggest that entropy of metals depend on electronic concentration. The trend display by metals in figure 1 also revealed that entropy of metals depends on statistical structure factor. Figure 2 shows variation of entropy at different temperature with electron density parameter for metals from different group and period. The trend demonstrated by metals in figure 2 revealed that entropy of metals increases as temperature increases, this could be due to an increase in kinetic energy between interacting electron which causes a high rate of electron disorderliness in metals and their-by forces the entropy of metals to increase as temperature increases. In figure 2 most of the metals whose entropy were computed and studied have more of their electron concentrated in region of

high-density limit than low-density limit. These seems to suggest that at any temperature, entropy of metal depend on ratio of valence electrons to number of their atoms. Figure 3 shows variation of entropy with strain for metals from different groups and periods. Figure 3 revealed that entropy of metals increases as deformation/strain increases with metals in the region of high-density limit having low entropy while metals in the region of low density limit have higher entropy. The increase in entropy as strain rises can be due to reduction in electron internal vibrational energy which forces the electron disorder rate to increase and then give rise to high entropy as strain increases. Potassium has highest entropy among all metals subjected to different deformation due to its low tensile strength as it cannot be stretched to some degree without breaking while Tungsten has lowest entropy among all metals subjected to different deformation due to its high tensile strength as it can be stretched to some degree without breaking. Another factor responsible for entropy increase as strain increase in figure 3 could be due to an increase in temperature between interacting electrons in metals. An increase in temperature gives electron in metals more kinetic energy as fast moving electrons causes more disorder than those moving slowly.

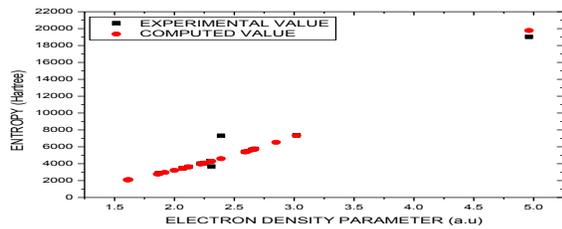


Figure 1: Variation of Entropy with Electron Density Parameter for some Metals

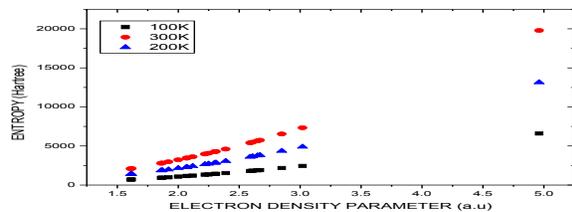


Figure 2: Variation of Entropy at Different Temperature with Electron Density Parameter for some Metals

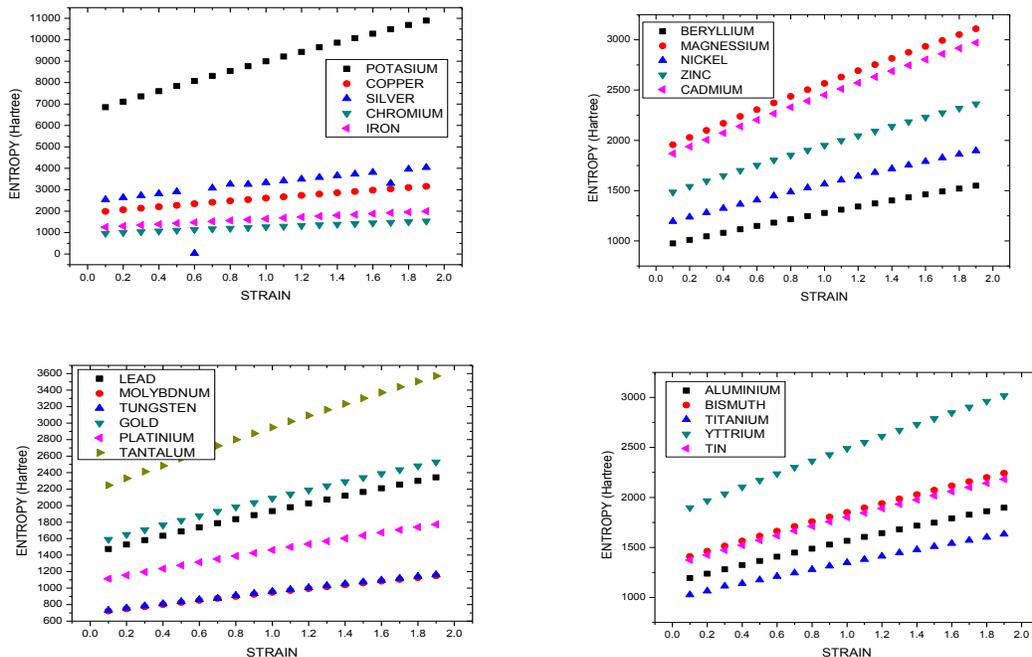


Figure 3: Variation of Entropy with Strain for some Metals

Table 1: Entropy of unstrained Metals.

Metals	Electron Density Parameter $r_s(a.u)$	Exp. Entropy (Hartree)	Computed Entropy (Hartree)
K	4.96	19024.4	19780.6
Cu	2.67	5762.05	5731.90
Ag	3.02	7358.49	7333.14
Be	1.87	2852.19	2811.64
Mg	2.65	5656.49	5646.35
Cr	1.86	-	2781.64
Fe	2.12	3633.24	3613.66
Ni	2.07	-	3445.22
Zn	2.31	3666.50	4290.42
Cd	2.59	5404.81	5393.56
Al	2.07	3467.48	3445.22
Bi	2.25	4073.67	4070.43
Ti	1.92	-	2964.00
Y	2.61	-	5477.18
Sn	2.22	4020.62	3962.61
Pb	2.30	4304.39	4253.35
Mo	1.61	-	2084.14
W	1.62	-	2110.11
Au	2.39	7318.52	4592.74
Pt	2.00	-	3216.15
Ta	2.84	-	6530.79

Table 2: Entropy of Deformed Metals

Metals	$r_s(a.u)$	Strain								
		0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8
K	4.96	7105.62	7599.34	8077.06	8540.63	8991.60	9431.20	9860.47	10280.3	10691.5
Cu	2.67	2059.02	2202.09	2340.53	2474.86	2605.53	2732.91	2857.31	2978.96	3098.13
Ag	3.02	2635.90	2817.25	31.4450	3259.01	3333.39	3496.36	3655.51	3811.17	3963.60
Be	1.87	1010.00	1080.18	1148.08	1213.98	1278.08	1340.57	1401.58	1461.26	1519.71
Mg	2.65	2028.29	2169.22	2305.59	2437.92	2566.65	2692.12	2814.67	2934.51	3051.89
Cr	1.86	999.229	1068.65	1135.84	1201.02	1264.44	1326.27	1386.63	1445.67	1503.49
Fe	2.12	1298.11	1388.30	1475.58	1560.26	1642.66	1722.89	1801.38	1878.08	1953.20
Ni	2.07	1237.60	1323.53	1406.80	1487.54	1566.09	1642.64	1717.42	1790.54	1862.15
Zn	2.31	1541.22	1648.30	1751.92	1852.47	1950.28	2045.64	2138.74	2229.81	2319.00
Cd	2.59	1937.49	2072.11	2202.36	2328.77	2451.73	2571.59	2688.64	2803.13	2915.26
Al	2.07	1237.60	1323.59	1406.80	1487.54	1566.09	1642.64	1717.42	1790.54	1862.15
Bi	2.25	1462.19	1563.79	1662.09	1757.49	1850.29	1939.59	2029.08	2115.42	2200.09
Ti	1.92	1064.73	1138.76	1210.30	1279.76	1347.34	1413.20	1477.53	1540.47	1602.07
Y	2.61	1967.52	2104.23	2236.51	2364.87	2489.75	2611.46	2730.33	2846.58	2960.44
Sn	2.22	1423.46	1522.37	1618.07	1710.94	1801.27	1889.34	1975.33	2059.45	2141.81
Pb	2.30	1527.90	1634.06	1736.78	1836.47	1933.44	2027.96	2120.26	2210.54	2298.96
Mo	1.61	748.668	800.688	851.022	899.872	947.383	993.700	1038.93	1083.16	1126.50
W	1.62	757.996	810.669	861.628	911.084	959.191	1006.08	1051.87	1096.66	1140.53
Au	2.39	1649.80	1764.45	1875.36	1983.01	2087.71	2189.78	2289.44	2386.93	2482.41
Pt	2.00	1155.31	1235.58	1313.25	1388.63	1461.95	1533.42	1603.22	1671.49	1738.35
Ta	2.84	2329.56	2483.27	2648.05	2800.04	2947.88	3092.01	3232.75	3370.40	3505.20

4.0 Conclusion

In summary, this report clearly explains entropy of metals as a function of electron density parameter and linearly applied strain/deformation. Entropy of metals are computed and studied based on the theory of free electron approximation using the knowledge of thermodynamic potentials. Result obtained agree quite well with theoretically obtained experimental value which shows the validity of the model used in this report. Entropy of metals depend on electronic concentration and statistical structure factor. Entropy of metals increase as temperature and deformation increases.

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