Theoretical Computation of Electron Critical Temperature of Metals based on Bardeen, Cooper Schriffer (BCS) Theory using Free Electron Approximation

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Abstract: In this paper, we apply Bardeen-Copper-Schrieffer (BCS) theory to the critical temperature of electron in metal using the theory of free electron approximation. The result obtained shows a good agreement between the computed and theoretically obtained experimental value for the electron critical temperature of metal. This agreement shows that free electron theory is useful in the study of some properties of metals. The parameter relating compression to elongation in the direction of applied strain is taking into consideration during the computation. Result obtained revealed that electron critical temperature depend on density of valence electron in metals. Most of the metals whose electron critical temperature were computed and studied have their electron concentrated in the region of high density limit than the low density limit. This suggest that the higher the density of valence electron in metals the higher the magnitude of intermolecular force of attraction between the electrons in metal and the higher the critical temperature of the electron in the metal. The critical temperature of electron in metal decreases as strain increases. This may be due to reduction in the magnitude of intermolecular force of attraction between the electrons in the metal as strain increases. The noble and transition metals has high electron critical temperature than alkaline metals when subjected to different strain. These may be due to the polyvalent nature of their valence electron and the electron bond scattering coefficient.

Introduction

Solid contains electrons, each element exists as either solid, liquid or gas at ambient temperature and pressure. Solid composed of a combination of elements listed in the periodic table Kittel (1976). In metals, there are electrons that do not belong to any particular group of atoms but rather are delocalized and extended throughout the system. These are conduction electrons that carry electric current when electric field is applied Elliott (1997). The atoms in metal also have core electrons which fill the inner shells and are local to each atom Animalu, (1977). The electron theory of metals describe the development of ideas that lead to the understanding of various properties manifested by different solid on the basis of electronic bonding among constituent atoms Uichiro (2003). In free electron model the allowed energy values are distributed essentially continuously from zero to infinity. This model answers almost all the qualitative questions about the behavior of electrons in metals Pillai (2010). Free electron model of metals gives good insight into the heat capacity, thermal conductivity, electrical conductivity, magnetic susceptibility, and electrodynamics of metals Ashcroft and Mermin (1976). The electronic structure of solid can be explored by analyzing the energy distribution of photoelectrons emitted upon irradiation of a sample by electromagnetic waves Kakani and Kakani (2004). Conduction electron in solid interact not only with an array of positive ions but also with other electrons. Bloch theorem plays a key role in describing the motion of the conduction electron in a periodic potential and explain how the free-electron E–k relation is perturbed by periodic potential Elliott (1997). Conductor are material that losses all its resistivity and has infinite conductivity. The electrical properties of solid depend

on electron band structure, i.e. the arrangement of outermost electrons in bands and the way in which they are filled with electrons Kakani and Kakani (2004). Superconductivity is the physics of Cooper Pairs, and superconducting state of metal exists only in a particular range of temperature and field strength. Superconductivity of metal disappear if the temperature of the specimen is raised above its critical temperature Kittel (1976). Cooper pair is bound state of two electrons with energy at the Fermi surface having spin and vector momentum of opposite sign. Cooper pairs is formed from electrons having parallel spins Kachhava (1992). Electrons repel each other in vacuum but under certain circumstances when in a crystal lattice they attract each other and form a Cooper pair. Critical temperature also called transition temperature is one of most important parameters characterizing superconductors Efthimios (2003). Critical pressure and temperature is the pressure and temperature at the critical point Madelung (1995). The highest temperature at which a materials remains superconducting is termed the critical temperature. Bardeen, Cooper and Schrieffer (BCS) relate a single "Cooper pair" with the many-electron theory and to cope with the overlap of many pairs. Bardeen, Cooper and Schrieffer BCS successfully constructed the wave function by taking a linear combination of many normal-state configurations in which the Bloch states are occupied by a pair of opposite momenta and spins Patterson and Bailey (2010). Once the attractive interaction between two electrons dominates over the repulsive screened Coulomb interaction, the system produce as many Cooper pairs as possible to lower its energy Madelung (1995). Bardeen, Cooper and Schrieffer BCS showed how this attractive interaction give rise to many-particle state which is lower in energy than the normal state by an amount proportional to $(\hbar\omega_D)^2$ in agreement with the isotope effect Rogalski and Palmer (2000). Bardeen, Cooper and Schrieffer BCS constructed the ground-state wave function in the superconducting state using a Hartree-like approximation and expressed it as a product of the individual Cooper pair wave functions Kakani and Kakani (2004). In Bardeen, Cooper and Schrieffer BCS theory, the energy gap remain unchanged even when a magnetic field is applied. This means that the density of the Cooper pairs and the ordered state remains unchanged Rogalski and Palmer (2000). Greatly increased computing power has allowed many ab initio methods of calculations to become practical and most of these require specialized discussions Lynton (1957) measures the threshold magnetic field as a function of temperature for specimens of tin containing impurities and obtained the superconductive critical temperature and temperature coefficient of electronic specific heat at normal phase. The change in critical temperature produced by the impurities decreases with an increase in

residual resistance ratio and a reduction in electronic mean free path. Results obtained also shows that the measurable changes in temperature coefficient are positive for all solutes indicating a minimum in the density of states near the Fermi energy. He also obtained a value of temperature coefficient for pure tin which agrees well with calorimetric result. Pop et.al, (2000) study the correlation between valence electron concentration (VEC) and the critical temperature for high-temperature superconductors. They found that for a certain class of compounds the critical temperature values are higher as the valence electron concentration. The critical temperature versus valence electron concentration linear curve extrapolation indicates the possible maximum critical temperature value which could be theoretically obtained for Bi- and Tl-based superconductors. Tarazewicz (2013) investigated some factors affecting the critical temperature of a two-band model superconductivity using perturbation theory. Based on conventional Cooper pairs from a wider band and local pairs from a narrower band induced via a pair-exchange potential. Result obtained revealed that the Coulomb potential lower the critical temperature from higher values to the pure Bardeen, Cooper and Schrieffer BCS and a rapid increase of the critical temperature due to the strong effect of the presence of local electron pairs is observed. Hess (2006) estimated the critical temperature of tungsten and the number of free electron per atom using the critical values from a van der Waals-like equation of state modified for metals based on Coulomb interaction in the attractive part. He observed that a scaling of the critical temperature with the Plasmon energy also fits numerically in the estimation of critical temperature although there is a different dependence upon the electron density. Belli et.al (2021) analyze the structural and electronic properties of some predicted hydrogen-based superconductors and discovered that the capacity of creating an electronic bonding network between localized units is key to enhance the critical temperature in hydrogen-based superconductors. He also define the networking value which correlates with the predicted critical temperature better than any other descriptor by classifying the studied compounds according to their bonding nature. Westerdale (2010) studied the critical temperatures of some metals and their suppression in magnetic and critical field. Result obtained shows a persistent current in superconducting lead that held an initial internal zero flux and that many metals display special properties below a certain critical temperature when they become superconducting. In this paper, Bardeen, Cooper and Schrieffer BCS theory is extended to the study of electron critical temperature in metals using the knowledge of free electron approximation. The metals were chosen based on the availability of physical constants required for computation.

Theoretical Consideration

Consider two free electron in state $\vec{k}_1$ and $\vec{k}_2$ with energies $\hbar^2\vec{k}_1^2/2m_e$, $\hbar^2\vec{k}_2^2/2m_e$ and total momentum $\vec{K} = \vec{k}_1 + \vec{k}_2$, since electron pairs of opposite spin have a lower energy, cooper pairs will be formed by electrons of opposite spin and their spatial wave function must be symmetric under permutation of the electrons and can be written as

$$\Psi_0(\vec{r}_1, \vec{r}_2) = A\, expi(\vec{k}_1 \cdot \vec{r}_1 + \vec{k}_2 \cdot \vec{r}_2) = A\, expi(\vec{K} \cdot \vec{R} + \vec{k} \cdot \vec{r}) \qquad (1)$$

where A is normalization constant, $\vec{R} = (\vec{r}_1 + \vec{r}_2)/2$ denotes the position of the centre of mass of the pair, $\vec{r} = \vec{r}_1 - \vec{r}_2$ denotes the relative position of the two electrons with wave vector $\vec{k} = (\vec{k}_1 - \vec{k}_2)/2$. The energy of the pair corresponding to the state in equation (1) can be written as

$$E_0 = \frac{\hbar^2}{2m_e}(\vec{k}_1^2 + \vec{k}_2^2) = \frac{\hbar^2}{2m_e}\left(\frac{\vec{K}^2}{4} + \vec{k}^2\right) \qquad (2)$$

An electron pair at rest is described by taking $\vec{K} = 0$, which implies electron pairs with equal and opposite wave vectors $\vec{k} = \vec{k}_1 = -\vec{k}_2$ and energy $E_0 = \hbar^2\vec{k}^2/2m_e$ which have the state function

$$\Psi_0(\vec{k}, -\vec{k}) = \Psi_{\vec{k}}(\vec{r}_1 - \vec{r}_2) = \Psi_{\vec{k}}(\vec{r}) = A\, exp(i\vec{k} \cdot \vec{r}) \qquad (3)$$

In the presence of a weak attractive interaction $V(\vec{r}_1 - \vec{r}_2) < 0$ between the two electrons, the wave function of a pair must satisfy the energy eigenvalues equation

$$\left[-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 + V(\vec{r}_1 - \vec{r}_2)\right]\Psi(\vec{r}_1 - \vec{r}_2) = E\Psi(\vec{r}_1 - \vec{r}_2) \qquad (4)$$

which reduces to

$$[(E_0 - E) + V(r)]\Psi(r) = 0 \qquad (5)$$

where $\vec{r} = \vec{r}_1 - \vec{r}_2$ and E_0 is the energy of the pair in the absence of interaction. A trial solution of equation (5) is a linear combination of the unperturbed pair states in equation (3) is

$$\Psi(\vec{r}_1 - \vec{r}_2) = \sum_{\vec{k}} a_{\vec{k}} A\, exp(i\vec{k} \cdot \vec{r}) \qquad (6)$$

Since the electron-electron interaction is postulated as an exchange of phonons where a phonon can assume a maximum energy $\hbar\omega_D$ limited by the Debye frequency $\omega_D = v\left(6\pi^2\frac{N}{V}\right)^{1/3}$, the summation must be restricted in equation (6) to values in the range

$$\varepsilon_f < \frac{\hbar^2\vec{k}^2}{2m_e} < \varepsilon_f + \hbar\omega_D \qquad (7)$$

This restriction is consistent with the situation where all the one-electron states with wave vector $\vec{k}$ within the Fermi sphere are filled at T=0 and all the states of energy higher than $\varepsilon_f(0)$ are empty. The states which do not comply with the restriction in equation (7) where $\varepsilon_f \equiv \varepsilon_f(0)$ for low temperatures are considered not to be directly involved in the superconducting transition. Usually $\hbar\omega_D \ll \varepsilon_f$.

Substituting equation (6) into equation (5), multiplying by $exp(i\vec{k} \cdot \vec{r})$ and integrating over the normalization volume V gives

$$(E_0 - E)a_{\vec{k}} + \sum_{\vec{k}'} a_{\vec{k}'} \int V(\vec{r})e^{i(\vec{k}-\vec{k}')\vec{r}}\, dV = 0 \qquad (8)$$

The electron-electron interaction $V(\vec{r})$ scatter the electron pair from a state $\Psi(\vec{k}, -\vec{k})$ to a state $\Psi(\vec{k}', -\vec{k}')$. The scattering matrix element is replaced in the Bardeen, Cooper-Schrieffer (BCS) theory by an average value $-V_0$ independent of $\vec{k}$ for $\vec{k}$ −state within the range specified by equation (7). This is called weak-interaction approximation which allows us to rewrite equation (8) in the form

$$(E_0 - E)a_{\vec{k}} = V_0 \sum_{\vec{k}'} a_{\vec{k}'} = C \qquad (9)$$

where C is independent of $\vec{k}$. Summing equation (9) over $\vec{k}$ we obtain

$$\sum_{\vec{k}} a_{\vec{k}} = C \sum_{\vec{k}} \frac{1}{E_0 - E} \qquad (10)$$

In view of equation (9)

$$\frac{1}{V_0} = \sum_{\vec{k}} \frac{1}{E_0 - E} \qquad (11)$$

The sum over $\vec{k}$ which extends over all electron pair states compatible with the restriction in equation (7) can be replaced in equation (11) by an integral

$$\frac{1}{V_0} = \int_{\varepsilon_f}^{\varepsilon_f + \hbar\omega_D} \frac{f(E_0)dE_0}{E_0 - E} \qquad (12)$$

where $f(E_0)$ is the density of pair states. Since the range of interaction is small compared to ε_f, we may replace $f(E_0)$ by $f(\varepsilon_f)$ which can be taken out of the integral so that equation (12) becomes

$$\frac{1}{V_0 f(\varepsilon_f)} = \int_{\varepsilon_f}^{\varepsilon_f + \hbar\omega_D} \frac{dE_0}{E_0 - E} = ln\frac{\varepsilon_f + \hbar\omega_D - E}{\varepsilon_f - E} = ln\left(1 + \frac{\hbar\omega_D}{\varepsilon_f - E}\right) \qquad (13)$$

It is convenient to express the binding energy of the pair defined by

$$2\Delta = 2\varepsilon_f - E \qquad (14)$$

in terms of the density of one-electron states at the Fermi level $N(\varepsilon_f)$ which is the same as the density of pair states at $2\varepsilon_f$, $f(2\varepsilon_f)$. Then it follows from equation (13) that

$$2\Delta = \frac{2\hbar\omega_D}{\exp\left(\frac{1}{V_0 N(\varepsilon_f)-1}\right)} \qquad (15)$$

which shows that the pair state $\Psi(\vec{r}_1 - \vec{r}_2)$ in equation (6) corresponds to a pair of electrons with energy E which is lower than $2\varepsilon_f$ by 2Δ. In other words, pairs of electrons with antiparallel spins form bound states near the Fermi energy. In the weak interaction approximation we have $V_0 N(\varepsilon_f) \ll 1$ so that

$$\Delta \equiv \hbar\omega_D \exp\left(-\frac{1}{V_0 N(\varepsilon_f)}\right) \qquad (16)$$

Taking $\Delta \sim k_B T$ and $\hbar\omega_D = k_B\theta_D$. Where θ_D is Debye temperature given by

$$\theta_D = \frac{\hbar\omega_D}{k_B} = \frac{\hbar v}{k_B}\left(6\pi^2 \frac{N}{V}\right)^{1/3} \qquad (17)$$

An estimate of the critical temperature in terms of the Debye temperature of a superconducting solid is obtained as

$$T_c = \theta_D \exp\left(-\frac{1}{V_0 N(\varepsilon_f)}\right) \qquad (18)$$

Inserting equation (17) into (18) gives

$$T_c = \frac{\hbar v}{k_B}\left(6\pi^2 \frac{N}{V}\right)^{1/3} \exp\left(-\frac{1}{V_0 N(\varepsilon_f)}\right) \qquad (19)$$

Where $\frac{N}{V}$ is electronic concentration, v is average speed of sound, v_F is the Fermi speed, k_F is Fermi wave-vector, $N(\varepsilon_f)$ is the density of state and V_0 is the effective coupling. In this paper, the critical temperature of electron in elemental metals were computed using equation (19). The metals were selected based on the availability of physical constant require for computation.

Results and Discussion

Figure 1 shows the plot of electron density parameter dependence of critical temperature of electron in pure metals. Figure 1 revealed that critical temperature of electron in metal decreases as the electron density parameter increases with metals in the region of high density limit having high value of electron critical temperature while metals in the region of low density limit has low values of electron critical temperature. This may be due to high conduction electrons per unit volume that is found in metals in the region of high density limit and low value of conduction electrons per unit volume that is found in metals in the region of low density limit. The result obtained in figure 1 revealed that there is a good agreement between the computed and theoretically obtained experimental value for the electron critical temperature of metal. These agreement is due to the validity of the model used for computation with the free electron theory. The trend demonstrated by metals in figure 1 also shows that electron critical temperature of metals depend on density of valence electron as metals whose electron critical temperature were computed and studied have most of their electron critical temperature concentrated in the region of high density limit than the low density limit. Another reason that could be responsible for the high electron critical temperature that is found in metal in the region of high density limit in figure 1 could be due to the fact that the higher the density of valence electron in metals the higher the magnitude of intermolecular force of attraction between the electron in the metals. Figure 2 shows the plot of strain dependence of electron critical temperature in pure metals. Figure 2 revealed that the critical temperature of electron in metal decreases as strain increases for all the metals. This decrease in electron critical temperature may be due to reduction in the magnitude of intermolecular force of attraction between the electrons in metal as strain increases. Among all metals subjected to different strain, Molybdenum and Tungsten has the highest electron critical temperature, this may be due to their high complex cuprate oxide, polyvalent nature and magnitude of intermolecular forces between their valence electron. Potassium has the lowest electron critical temperature as it may be due to their alkaline nature as monovalent metals is an excellent conductors of electricity at ambient temperatures. Furthermore, the decrease in the electron critical temperature as the strain increases in figure 2 may be due to the fact that as strain increases, the interatomic spacing between the electron in metals increases which then weaken dipole interaction between the valence electron in the metals and then forces the electron critical temperature to decrease as the strain increases. Another thing that can be responsible for the low values of the critical temperature of Potassium when subjected to different strain could be due to the nature of bonding between the atoms and ion core electrons. In figure 2, most of the metals subjected to different strain exhibit curved shape except potassium that exhibit a straight line shape. This may be due to the nature of Potassium electronic band structure and electronic strength.

Conclusion

Critical temperature of electron in metals is computed and studied based on Bardeen-Copper-Schrieffer (BCS) theory using the knowledge of free electron theory. The parameter relating the ratio of lateral strain to longitudinal strain in the direction of applied strain is taking into consideration during the computation. Results obtained revealed that critical temperature of electron in metal decreases as the electron density parameter increases with metals in the region of high density limit having high value of electron critical temperature while metals in the region of low density limit were having low values of electron critical temperature. The critical temperature of electron in metal decreases as strain increases. As strain increases the inter atomic distance between the electron in metal increases and their-by reduces the strength of the intermolecular interactions that hold the electron in metals together and then forces the electron critical temperature in metals to decrease as strain increases.

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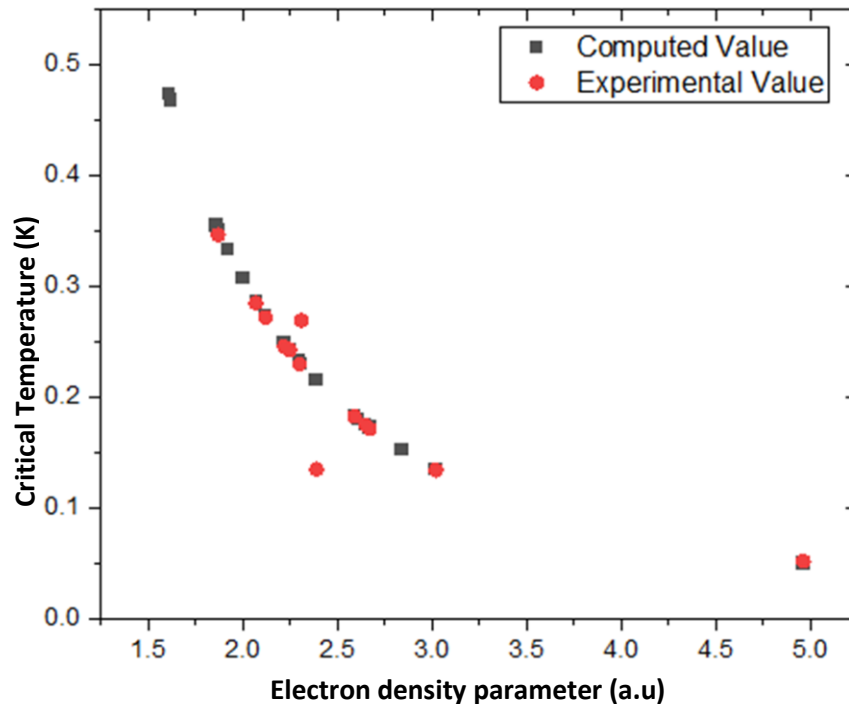
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Figure 1: Plot of Electron Density Parameter Dependence of Critical Temperature in Pure Metal
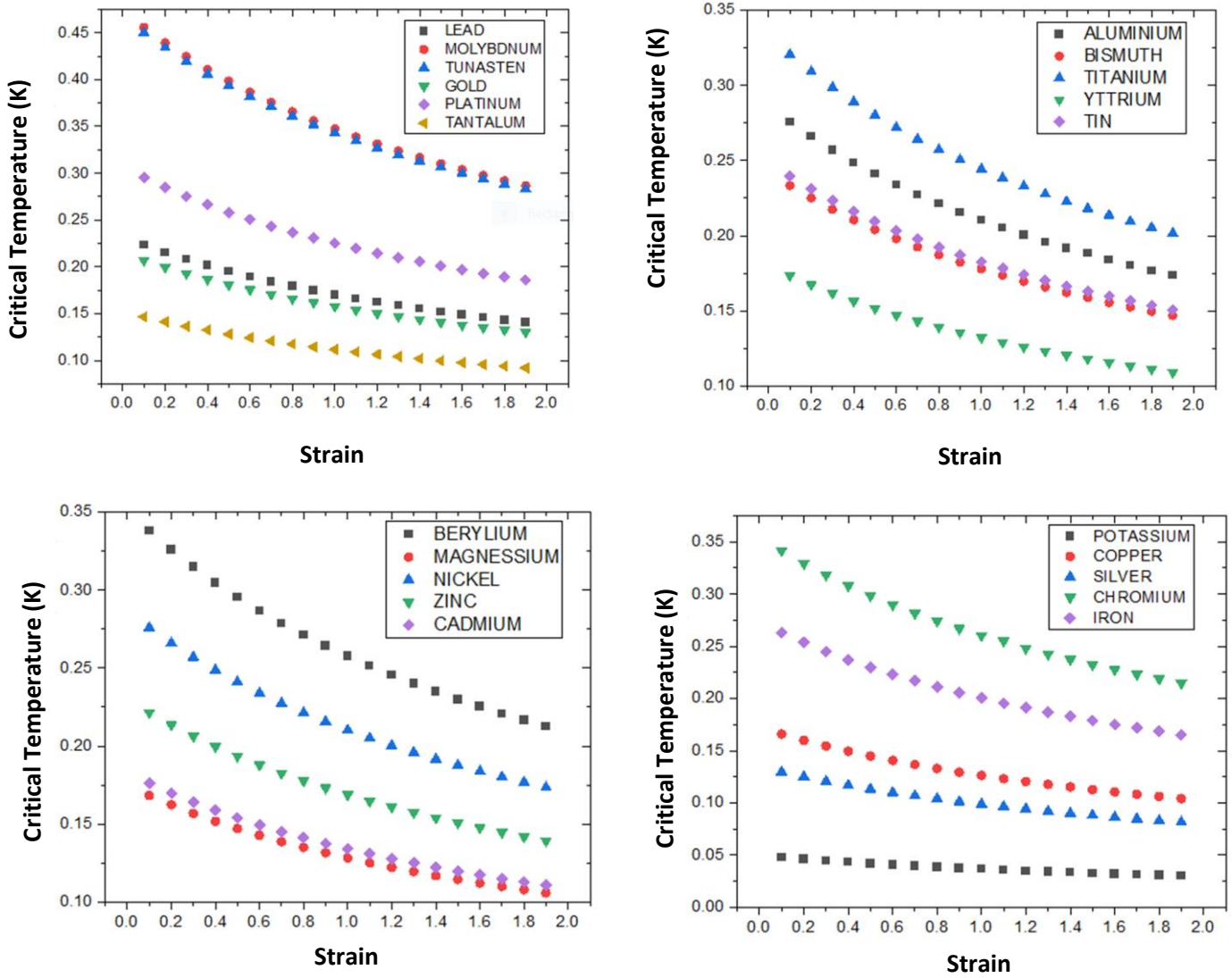
Figure 2: Plot of Strain Dependence of Critical Temperature in Pure Metals

Table 1: Critical Temperature of Unstrained Metals

Metals	Electron Density Parameter r_s(a.u)	Critical Temperature (K)	
		Experimental Value	**Computed Value**
K	4.96	5.193333E-02	4.991545E-02
Cu	2.67	0.171467	0.172257
Ag	3.02	0.134267	0.134643
Be	1.87	0.346400	0.351168
Mg	2.65	0.174667	0.174866
Cr	1.86	-	0.354954
Fe	2.12	0.271933	0.273229
Ni	2.07	-	0.286588
Zn	2.31	0.269533	0.230131
Cd	2.59	0.182800	0.183062
Al	2.07	0.284933	0.286588
Bi	2.25	0.242533	0.242568
Ti	1.92	-	0.333116
Y	2.61	-	0.180267
Sn	2.22	0.245733	0.249168
Pb	2.30	0.229533	0.232136
Mo	1.61	-	0.473747
W	1.62	-	0.467916
Au	2.39	0.135000	0.214982
Pt	2.00	-	0.307000
Ta	2.84	-	0.152252

Table 2: Critical Temperature of Strained 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	0.0463	0.0433	0.0407	0.0385	0.0366	0.03489	0.0334	0.0320	0.0308
Cu	2.67	0.1598	0.1495	0.1406	0.1330	0.1263	0.1204	0.1152	0.1105	0.1062
Ag	3.02	0.1249	0.1168	0.1099	0.1039	0.09873	0.09413	0.09003	0.08636	0.08304
Be	1.87	0.3259	0.3047	0.2867	0.2711	0.2575	0.2455	0.2348	0.2252	0.2166
Mg	2.65	0.1623	0.1517	0.1427	0.1350	0.1282	0.1223	0.1169	0.1122	0.1078
Cr	1.86	0.3294	0.3080	0.2898	0.2740	0.2603	0.2482	0.2374	0.2277	0.2189
Fe	2.12	0.2535	0.2371	0.2230	0.2109	0.2004	0.1910	0.1827	0.1752	0.1685
Ni	2.07	0.2659	0.2487	0.2339	0.2213	0.2102	0.2004	0.1916	0.1838	0.1767
Zn	2.31	0.2135	0.1997	0.1879	0.1777	0.1688	0.1609	0.1539	0.1476	0.1419
Cd	2.59	0.1699	0.1588	0.1494	0.1413	0.1342	0.1280	0.1224	0.1174	0.1129
Al	2.07	0.2659	0.2487	0.2339	0.2213	0.2102	0.2004	0.1916	0.1838	0.1767
Bi	2.25	0.2251	0.2105	0.1980	0.1873	0.1779	0.1696	0.1622	0.1556	0.1496
Ti	1.92	0.3091	0.2890	0.2719	0.2572	0.2443	0.2329	0.2228	0.2137	0.2054
Y	2.61	0.1673	0.1564	0.1472	0.1392	0.1322	0.1260	0.1205	0.1156	0.1112
Sn	2.22	0.2312	0.2162	0.2034	0.1924	0.1827	0.1742	0.1666	0.1598	0.1537
Pb	2.30	0.2154	0.2014	0.1895	0.1792	0.1702	0.1623	0.1552	0.1489	0.1432
Mo	1.61	0.4396	0.4110	0.3867	0.3657	0.3474	0.3312	0.3168	0.3039	0.2922
W	1.62	0.4342	0.4060	0.3820	0.3612	0.3431	0.3271	0.3129	0.3001	0.2886
Au	2.39	0.1995	0.1865	0.1755	0.1660	0.1576	0.1503	0.1438	0.1379	0.1326
Pt	2.00	0.2849	0.2664	0.2506	0.2370	0.2251	0.2146	0.2053	0.1969	0.1893
Ta	2.84	0.1413	0.1325	0.1243	0.1175	0.1116	0.1064	0.1018	0.0976	0.0939

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