



A Theoretical Report on Electronic Polarizability of Metals

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Abstract

This paper reports the electronic polarizability of some metals from different groups and periods. The study revealed that electronic polarizability of metals increases as the electron density parameters increases. This could be due to high ratio of valence electron in metals to their number of atoms. Electronic polarizability of metals increases with an increase in electron density parameter because the outer shells electrons in multi-electronic atoms are less bonded to the nuclei having a higher contribution to electronic polarizability. These results indicate that free electron theory formalism is useful for theoretical calculation of some properties of metals as the electronic polarizabilities obtained in this work agreed quite well with the theoretically obtained experimental value. Electronic polarizability of all metals computed and studied increases as strain increases due to an increase in surface area, ionization energy, atomic radius and increase in distance between interacting electrons.

1.0. Introduction

Metals achieve structural stability by letting their valence electrons roam freely through the crystal lattice. These valence electrons are the equivalents of the molecules of an ordinary gas. Solid consists of a sufficiently large collection of atoms that exhibit the characteristic behavior of bulk material, the atom may lose some of its tightly bound electrons leaving the core electrons, such entity is known as ions [1]. Deformation is the change in shape or size of solid due to applied stress (force) or strain [2]. Metals could be deformed by a compressive, elongative and torsion/twisting force [3]. Dielectric material has interesting electrical properties because of the ability of an electric field to polarize the material and create electric dipoles [4]. Dielectrics are poor conductor of electricity. Dielectrics does not have free electric charges under ordinary circumstances [5]. Most important property of dielectrics is their ability to become polarized under the action of an external electric field. The process of producing electric dipoles out of neutral atoms and molecules is called polarization [6]. The number of lines of forces received per unit area is called flux density or electric displacement [5]. Polarizability is the ability of matter to acquire an electric dipole moment in proportion to that applied field when subjected to an electric field. The polarizability of an atom is the ratio of its induced dipole moment to the local electric field [7]. Electric polarizability describes the relative tendency of a charge distribution to be distorted from its normal shape by an external electric field [4]. Electronic polarizability captures the dielectric nature of material which is united to other physical quantities in an atomically thin layer [8]. Electronic polarization occurs

due to displacement of the centre of the negatively charged electron cloud relative to the positive nucleus of an atom by the electric field [7]. Electronic Polarizability is proportional to the volume of atoms and independent of temperature [1]. Atoms in a set of molecules imposed to an external electric field undergo displacements from their equilibrium positions giving rise to atomic polarizability [9]. In addition, charge carriers that migrate some distance in dielectric contribute to polarization [10]. [11] developed a model for estimating the dielectric constant due to electronic polarization using a semiempirical molecular orbital method. The calculated dielectric constants were in agreement with experimental data when compared. A linear relationship that is useful in estimating the experimental dielectric constant due to electronic polarization is obtained. [12] computed the electronic polarizabilities of ions in alkali chalcogenide crystals using a relationship according to which the electronic polarizability of an ion should vary as the cube of its radius. The polarizabilities obtained are in close agreement with result obtained from experimental refraction data by other researchers. [13] employed the continuum dielectric model for electronic polarizability, and developed a new consistent procedure for parameterization of the effective nonpolarizable potential of liquid water using Kirkwood - Onsager theory. Result obtained is fully consistent with experimental data on enthalpy of vaporization, density, diffusion coefficient and static dielectric constant. The new theoretical framework provides important insights into the nature of effective parameters which is crucial when the computational models of liquid water are used for simulations in different environment. [14] studied the effect of self-interaction error (SIE) on the static dipole polarizabilities of water clusters modeled with three increasingly sophisticated, non-empirical density functional approximations (DFA), based on the local spin density approximation (LDA), Perdew–Burke–Ernzerhof (PBE), generalized-gradient approximation (GGA) and strongly constrained and appropriately normed (SCAN) meta-GGA, using the Perdew–Zunger self-interaction-correction (PZ-SIC) energy functional in the Fermi–Lowdin orbital SIC framework. Results obtained shows that the density functional approximation overestimate the cluster polarizabilities, the description systematically improves from LDA to PBE to SCAN. The self-correlation free SCAN predicts polarizabilities quite accurately with a mean absolute error (MAE) with respect to coupled cluster singles and doubles (CCSD) values. And the LSIC polarizabilities are in excellent agreement with most recent coupled cluster singles and doubles polarizabilities. [15] study the static and dynamic electronic polarizability of benzonitrile using refraction index measurements of neat benzonitrile and CCl₄, THF, C₆H₁₂ and CH₃CN diluted solutions. Results obtained indicate that the vibrational contribution to the visible refraction is very small, and the electronic polarizabilities calculated with these values agree with reported values. The polarizabilities obtained in this work agree well with theoretical and experimental data, reported by other authors. The static and dynamic electronic polarizability of benzonitrile was found to be little affected by the dielectric nature of the solvent, and the electric deformability is similar to that of the benzene molecule. The effect of the replacement of the C—H group by N in 4-cyano-pyridine and benzonitrile molecules is discussed. [16] presented the temperature dependence of density, refractive indices and dielectric constant of three samples of crude oils. The measured data of refractive index and the density are used to evaluate the polarizability of these fluids. Molar refractive index and the molar volume are evaluated through Lorentz-Lorentz equation. The measured values of the dielectric constant decrease linearly with increasing temperature for all the samples. The dielectric constant estimated from the refractive index measurements using Lorentz-Lorentz equation agrees well with the measured values. This result offers a simple and reliable method for estimating crude oil properties, in the absence of sufficient data. [17] discussed the current status of the development of the optical basicity concept and Sun's approach on single bond strength to Bi₂O₃-B₂O₃, ZnO-Bi₂O₃-B₂O₃ and R₂O-B₂O₃-SiO₂ (R = Li, Na and K) glasses. They reported that the optical basicity increases with decreasing average single bond strength in all glass system. More acidic glasses possess large BM-O(480 - 320kJ/mol) which means participation of an average oxide ion in more covalent M-BO (bridging oxygen) bonds such as B-O-B and Si-O-

Si. The smallest values of BM-O about 300 - 250 kJ/mol have been obtained for bismuthate glasses. It has been assumed that these values support the formation of Bi-O-B, Bi-O-Bi, Zn-O-B and Zn-O-Bi bonds with increased ionicity. [18] reported that the refractive index was determined through the optical electronegativity and obtained a perfect linear correlation between the calculated refractive index and the estimated values using the dielectric constant value of the prepared samples. The average electronic oxide polarizability and the interaction parameter of our ternary oxide glasses have been estimated on the basis of the average optical electronegativity. They reported that the estimated values are in good agreement with the available experimental data.

2.0. Theoretical Consideration

The screen electron-electron interaction problem can be treated from dielectric behavior of electron gas under an external perturbation with a homogenous non interacting electron of concentration $n = \frac{N}{V_g}$ by applying an external perturbation $V_a(r, t)$, fluctuations in the electron gas are induced ($n = n_o + \delta n$) which are connected with an internal potential through the Poisson equation

$$\nabla^2 V_i(r, t) = -\frac{e^2}{\epsilon_o} \delta n(r, t) \quad (1)$$

where V_i describes the screening effect of the electron gas on an electron at point r , e is electronic charge and ϵ_o is permittivity of free space.

The equilibrium state of electron gas is described by statistical operator ρ_o as

$$\rho_N = Z_N^{-1} \exp\left(-\frac{H-\mu N_{OP}}{K_B T}\right) \quad (2)$$

where

$$Z = \sum_n \langle n | \exp\left(\frac{H-\mu N_{OP}}{K_B T}\right) | n \rangle = \text{Trace} \left\{ \exp\left(\frac{H-\mu N_{OP}}{K_B T}\right) \right\} \quad (3)$$

The probability that in a closed system a subsystem occupies a quantum state E_n is the Gibbs distribution given as

$$W_n = Z^{-1} \exp\left(-\frac{E_n}{K_B T}\right) \quad (4)$$

where z is a canonical partition function, K_B is Boltzmann constant and T is the temperature. The canonical partition function is connected with free energy by

$$Z = \exp\left(-\frac{F}{K_B T}\right) \quad (5)$$

The statistical mean values for all quantities which characterize the subsystem is

$$\bar{f} = \sum f_n W_n = Z^{-1} \exp\left(-\frac{E_n}{K_B T}\right) \quad (6)$$

Replacing equation (4) and (5) with the probability that the subsystem will be in the n th state and contain N particles, then

$$\left. \begin{aligned} W_n N &= Z_N^{-1} \exp\left(-\frac{E_n N - \mu N}{K_B T}\right) \\ Z_N &= \sum_{nN} \exp\left(-\frac{E_n N - \mu N}{K_B T}\right) \end{aligned} \right\} \quad (7)$$

where μ is the chemical potential, Z_N is the grand partition function is connected with the thermodynamic potential $\eta = F - \mu N$ in the same way as Z with the free energy

$$Z_N = \exp\left(-\frac{\eta}{K_B T}\right)$$

The statistical operator in equation (2) become

$$\rho_N = Z_N^{-1} \exp\left(-\frac{H - \mu N_{op}}{K_B T}\right) \quad (8)$$

The partition function in the occupation number becomes

$$Z_k = \sum_{nk} \exp\left(-\frac{E(k) - \mu N}{K_B T} nk\right) = 1 + \exp\left(-\frac{E(k) - \mu N}{K_B T}\right) \quad (9)$$

And the statistical operator in the occupation number representation is

$$\rho_k = Z_k^{-1} \exp\left(-\frac{E(k) - \mu N}{K_B T} C_k^+ C_k\right) \quad (10)$$

The average number of particles n_k in state k is

$$n_k = \text{Trace}[n_k \rho_k] = \sum_{nk} \langle n_k | n_k \rho_k | nk \rangle = \langle 1 | \rho_k | 1 \rangle \quad (11)$$

Applying Gauss theorem to a parallel plate condenser without a dielectric, the electric field E_o is

$$\int E_o dA = \frac{q}{\epsilon_o} \quad (12)$$

$$\text{where } E_o = \frac{q}{A \epsilon_o} \quad (13)$$

when dielectric is present, the net charge is $q - q'$ where q' is induced surface charge and the field is given by

$$\int E dA = \frac{q - q'}{\epsilon_o} \quad (14)$$

$$\text{where } E = \frac{q}{A \epsilon_o} - \frac{q'}{A \epsilon_o} \quad (15)$$

Equation (15) shows that induced charge q' tends to weaken the original field (i.e. $E < E_o$) which reveals itself as a reduction in the potential difference when dielectric is present and not present, then

$$\frac{E}{E_o} = \frac{V_o}{E_d} \quad (16)$$

where

$$\epsilon_r = \frac{V_o}{E_d}$$

Equation (16) becomes

$$\frac{E_o}{E} = \epsilon_r \quad (17)$$

$$E = \frac{E_o}{\epsilon_r}$$

Substituting for E_o from equation (13), we get

$$E = \frac{E_o}{\epsilon_r} = \frac{q}{A\epsilon_o\epsilon_r} \quad (18)$$

Comparing equation (18) with equation (15), we get

$$\frac{q}{A\epsilon_o\epsilon_r} = \frac{q}{A\epsilon_o} - \frac{q'}{A\epsilon_o} \quad (19)$$

then

$$q - q' = \frac{q}{\epsilon_r} \quad (20)$$

This indicates that the induced charge q' is less than the free charge q and is zero when $\epsilon_r = 1$ or when dielectric is absent. If q is the charge on the plate and q' is the induced charge on the boundary of the dielectric, then equation (19) can be written as

$$\frac{q}{A} = \frac{q}{A\epsilon_r} + \frac{q'}{A}$$

therefore,

$$\frac{q}{A} = \epsilon_o \left| \frac{q}{A\epsilon_o\epsilon_r} \right| + \frac{q'}{A} \quad (21)$$

The last term in equation (21) gives induced surface charge per unit area called electric polarization P .

Substituting equation (18) into equation (21), we get

$$\frac{q}{A} = E\epsilon_o + P$$

where

$$D = E\epsilon_o + P \quad (22)$$

Hence, $D = \frac{q}{A}$ is the electric displacement and polarization P is given as

$$P = \epsilon_o\chi E \quad (23)$$

where E is electric field and χ is electric susceptibility obtained as

$$\chi = \epsilon_r - 1 = n^{1/2} - 1 \quad (24)$$

where ϵ_r is relative permittivity and n is the refractive index. In free space where there is no dielectric $P = 0$, equation (22) becomes

$$D = \epsilon_o E$$

The electronic polarizability α is obtained as

$$\alpha = \frac{\epsilon_o(\epsilon_r - 1)}{N} = \frac{\epsilon_o\chi}{N} \quad (25)$$

where N is the number of atoms/ m^3 and ϵ_r is relative permittivity.

3.0. Results and Discussion

Figure 1 shows the plot of electronic polarizability with electron density parameter for metals from different groups and periods. Figure 1 shows that electronic polarizability of metals increases with an increase in electron density parameter. This revealed that electronic polarizability of metals increases with an increase in the number of electrons, since the outer shells' electrons in multi-electronic atoms are less bonded to the nuclei having a higher contribution to electronic

polarizability. The trend display by metals in Figure 1 may also be due to electronic polarizability dynamical response to bound external electric field. Figure 1 revealed that both computed and theoretically obtained experimental value agree with each other as they both exhibit a particular inward parabolic linear curve. The experimental value for the electronic polarizability is obtained theoretically by substituting directly the experimental value of Fermi energy obtained in Solid State Physics by [4] into the model used for computation. The trend display by metal in Figure 1 may also be due to the facts that metals in the region of low density limit has greater number of electron than metals in the region of high density limit which causes the electronic polarizability of metals in the low density region to be higher than those in the region of high density limit. Figure 2 shows the plot of electronic polarizability with strain for metals belonging to different groups and periods. Figure 2 revealed that electronic polarizability of all metals computed and studied increases as strain increases.

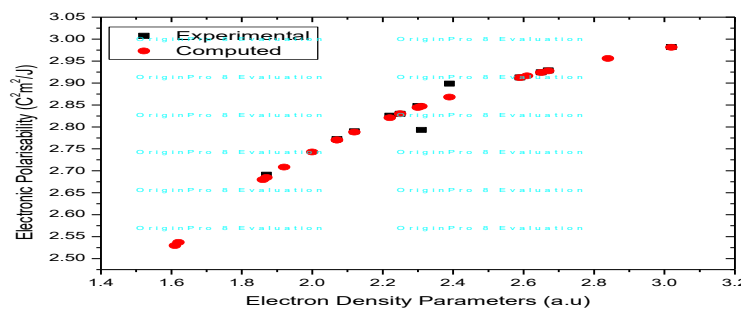


Figure 1: Variation of Electronic Polarizability with Electron Density Parameter of Metals

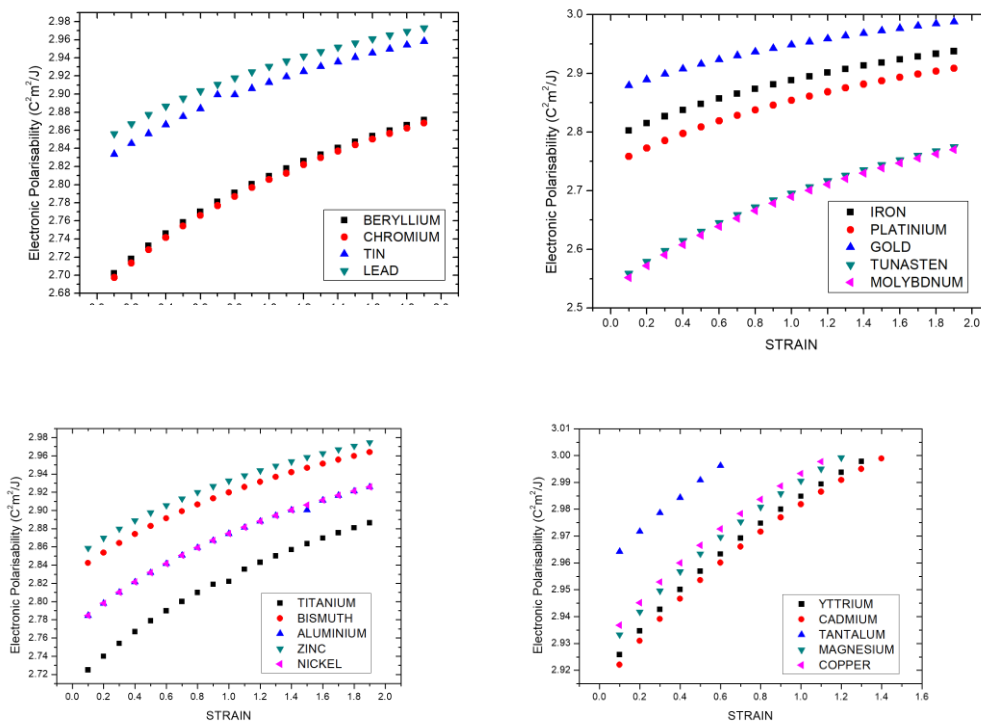


Figure 2: Variation of Electronic polarizability with

This may be due to an increase in surface area, ionization energy, atomic radius and increase in distance between electrons in metals that forces the electronic polarizability of metals to increase as strain increases. Apart from this, another thing that can also be responsible for the increase in electronic polarizability as the strain increases could be due to an increase in atomic defect characterized by relative displacements of electrons from their mean position, distortional and orientational electron defect in the metals. In conclusion, electronic polarizability of metals is highly affected by strain (deformation).

Table 1: Electronic Polarizability of Undeformed Metals

Metals	Electron Density Parameter $r_s(\text{a.u})$	Electronic Polarization ($\text{C}^2\text{m}^2/\text{J}$)	
		Experimental Values	Computed Values
Cu	2.67	2.92862	2.92759
Ag	3.02	2.98180	2.98128
Be	1.87	2.69096	2.68487
Mg	2.65	2.92412	2.92390
Cr	1.86	-	2.67995
Fe	2.12	2.78978	2.78812
Ni	2.07	-	2.77016
Zn	2.31	2.79309	2.84684
Cd	2.59	2.91271	2.91235
Al	2.07	2.77231	2.77016
Bi	2.25	2.82974	2.82977
Ti	1.92	-	2.70845
Y	2.61	-	2.91628
Sn	2.22	2.82538	2.82076
Pb	2.30	2.84756	2.84408
Mo	1.61	-	2.52973
W	1.62	-	2.53692
Au	2.39	2.89848	2.86776
Pt	2.00	-	2.74293
Ta	2.84	-	2.95603

Table 2: Electronic Polarizability of Deformed Metals

Metal	r_s (a.u)	Strain								
		0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8
Cu	2.67	2.94521	2.96002	2.97269	2.98367	2.99330	-	-	-	-
Be	1.87	2.71799	2.74600	2.77005	2.79098	2.80940	2.82575	2.84039	2.85359	2.86557
Mg	2.65	2.94176	2.95678	2.96963	2.98077	2.99054	2.99918	-	-	-
Cr	1.86	2.71337	2.74163	2.76591	2.78704	2.80563	2.82214	2.83692	2.85025	2.86233
Fe	2.12	2.81480	2.83731	2.85661	2.87337	2.88811	2.90116	2.91285	2.92337	2.93291
Ni	2.07	2.79798	2.82144	2.84159	2.85909	2.87446	2.88810	2.90031	2.91130	2.92126
Zn	2.31	2.86976	2.88906	2.90560	2.91995	2.93255	2.94372	2.95370	2.96268	2.97082
Cd	2.59	2.93097	2.94664	2.96005	2.97167	2.98186	2.99089	2.99895	-	-
Al	2.07	2.99895	2.82145	2.84159	2.85909	2.87446	2.88810	2.90031	2.91130	2.92126
Bi	2.25	2.85379	2.87404	2.89138	2.90644	2.91966	2.93138	2.94185	2.95128	2.95983
Ti	1.92	2.74012	2.76689	2.78987	2.80986	2.82204	2.84305	2.85702	2.86961	2.88103
Y	2.61	2.93465	2.95010	2.96331	2.97477	2.98482	2.99372	-	--	-
Sn	2.22	2.84536	2.86609	2.88386	2.89929	2.91284	2.92485	2.93559	2.94525	2.95401
Pb	2.30	2.86718	2.88664	2.90330	2.91777	2.93047	2.94173	2.95178	2.96084	2.96904

<i>Mo</i>	1.61	2.57209	2.60802	2.63897	2.66597	2.68978	2.71096	2.72996	2.74711	2.76270
<i>W</i>	1.62	2.57886	2.61443	2.64507	2.67180	2.69536	2.71632	2.73512	2.75209	2.76751
<i>Au</i>	2.39	2.88932	2.90747	2.92301	2.93650	2.94833	2.95882	2.96819	2.97662	2.98426
<i>Pt</i>	2.00	2.77245	2.79739	2.81879	2.83739	2.85374	2.86825	2.88124	2.89293	2.90354
<i>Ta</i>	2.84	2.97174	2.98432	2.99624	-	-	--	-	-	-

4.0. Conclusion

The present study suggests that electronic polarizability of metals increases as electron density parameter increases due to electronic polarizability dynamical response to bound external electric field. Electronic polarizability of all metals computed and studied increases as strain increases due to an increase in atomic defect characterized by relative displacements of electrons from their mean position and orientational electron defect in the metals. Thus, we conclude that electronic polarizability of metals is influence by strain (deformation) effect.

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