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Computation of Effective Debye Temperature of Liquid Metal Alloys

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***Abstract*: On the basics of quasicrystaline structure of liquid state Debye temperature, θD of two liquid metal alloys K-Rb and Na-Cs has been calculated at different temperatures ranging from (298.15–523.15) K and varying composition of alloys. Ultrasonic speed (u), density (ρ) and heat capacities ratio (γ) are the only data needed. Theoretical values have been compared with the standard finding and quite good agreement has been achieved. Experimental data of ρ, u and γ were taken from the literature. The negative values of ΔθD obtained are attributed to the decrease of short range order in the mixture compared to the order prevailing in pure liquid indicating less compression in mixture as compare to individual component. The mole ratios also affect the Debye temperature by decreasing its value with increase in the composition of the first component of the above two liquid metal alloys.**

***Index Terms*: Debye temperature, density, heat capacities ratio, liquid metal alloys, ultrasonic speed.**

I. INTRODUCTION

The concept of Debye temperature has been advanced by some workers (Kor, et al, 1974; Jain, et al, 1967; Pandey, et al, 1975; Pandey, 1979) during the year 1961-1975. Assuming the quasi-crystalline model for liquid (justified by cold mention scattering and other experimental techniques). The structure of a liquid can be denoted by the term quasi-crystalline in the sense that liquid displays a certain degree of local order of the same type as that of corresponding crystal. The study of dynamics of atomic motion of a liquid plays very important role in understanding the solid like behaviour of liquid. So, the name effective Debye temperature has been given. The effective Debye temperature of various types of pure liquids (Pandey, et al, 1976; Pandey, 1976; Pandey, et al, 1976), binary and higher order mixtures as well as for some liquid metals (Saxena, et al, 1975) has been computed, and structural studies of the systems were carried out through the Debye temperature. The theoretical approach has been modified by some workers (Vyas, et al, 2003; Pandey, et al, 2004). This enables to calculate θ_D using very limited input data. Further, the study of Debye temperature was extended to binary liquid mixtures (Pandey, 1979) and then to higher order liquid mixture (Pandey, et al, 2004; Magomedov, et al, 2018; Sinha, et al, 1989; Singh, et al, 2013; Mishra, et al, 2015). Due to the scarcity of experimental data, the effective Debye temperature of liquid metal alloys could not be calculated. However, using ultrasonic speed, density and heat capacities ratio, recently (Shukla, et al, 2007), θ_D has been computed for Sn-Pb alloy at different temperatures. In the present work, we are extending the calculation of θ_D to two alloys, namely K-Rb and Na-Cs at different temperatures. The experimental values of input data were taken from the literature (Kim, et al, 1971; Kim, et al, 1970).

II. THEORETICAL FORMULATION

Details of the theoretical formulation and modification are available in literature (Pandey, et al, 1975; Pandey, et al, 2004). Here, a brief account of formulae employed is presented. The expressive for effective Debye temperature, θ_D, is given by

$$\theta_D = \frac{h}{k}\left[\left(\frac{9N}{4\pi V}\right)\Big/\left(\frac{1}{C_t^3}+\frac{2}{C_l^3}\right)\right]^{\frac{1}{3}} \quad (1)$$

where h, k and N are Planck's constant, Boltzmann constant and Avogadro number respectively. V is the molar volume, C_t and C_l are respectively the transverse and longitudinal wave velocities.

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The Newton-Laplace equation is the starting point for the determination of isentropic compressibilities of medium using the speed of sound u and density ρ.

$$\beta_S = (u^2\rho)^{-1}$$

$$\beta_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$$, S is the entropy

Alternatively,

$$u = \sqrt{\frac{E_S}{\rho}}, \qquad E_S = \frac{1}{\beta_S}$$ = Adiabatic Elastic Modulity

The isentropic condition means that as the sound wave passes through a medium the pressure and temperature fluctuate within each microscopic volume but the entropy remains constant.

A modified expression (Pandey, et al, 2004; Singh, et al, 2017) for θ_D has been developed which can be written as

$$\theta_D = \frac{h}{k}\left[\frac{(9N/4\pi V)}{(\rho\beta_s)^{\frac{3}{2}}\left\{\left(\frac{1}{1+\gamma}\right)^{\frac{3}{2}} + 2\left(\frac{4}{3\gamma}\right)^{\frac{3}{2}}\right\}}\right] \quad (2)$$

where ρ and β_s are respectively the density and isentropic compressibility of liquid, γ is the heat capacities ratio given by

$$\gamma = \frac{C_P}{C_V} = \frac{\beta_T}{\beta_S}$$

Thus, the knowledge of γ and β_S, θ_D can be calculated. The ideal value of θ_D for liquid metal alloy is given by

$$(\theta_D)_{idl} = w_{metal(1)}(\theta_D)_{metal(1)} + w_{metal(2)}(\theta_D)_{metal(2)} \quad (3)$$

where $w_{metal(1)}$ and $w_{metal(2)}$ are respectively the weight fractions of metal-1 and metal-2, $(\theta_D)_{metal(1)}$ and $(\theta_D)_{metal(2)}$ are the values of θ_D for metal-1 and metal-2 respectively. The change in the value of θ_D on mixing of two pure liquid metals to form alloy is given by

$$(\theta_D)_D = (\theta_D)_{alloy} - (\theta_D)_{idl} \quad (4)$$

$$\Delta\theta_D = (\theta_D)_{alloy} - \left[w_{metal(1)}(\theta_D)_{metal(1)} + w_{metal(2)}(\theta_D)_{metal(2)}\right] \quad (5)$$

Knowing the values of $(\theta_D)_{metal(1)}$ and $(\theta_D)_{metal(2)}$, $\Delta\theta_D$ of alloy can be calculated.

III. RESULTS AND DISCUSSION

For the present study, depending on the input data, two liquid metal alloys, namely K-Rb and Na-Cs were considered. The experimental values of density (ρ), and ultrasonic speed (u) were taken from the paper of Kim and Letcher (Kim, et al, 1971). Calculation of θ_D has been extended over a wide range of temperature (298.15–523.15) K and at different composition of alloys. An alloy is treated as binary liquid mixture with the pure component liquids. Computed values of θ_D from eq (1) are recorded in Table I and Table II for K-Rb and Na-Cs alloys respectively.

Table I. Temperature and composition dependence of Debye temperature (θ_D) for K-Rb alloy.

T (K)	x=0(Rb)	0.197	0.340	0.510	0.594	0.710	0.821	0.862	0.95	1.00
298.15	81.3	84.7	87.6	92.7	95.6	101.3	109.3	110.7	117.5	131.8
323.15	80.8	84.3	87.1	92.1	95.1	100.7	108.7	110.0	117.0	131.1
348.15	80.3	83.9	86.6	91.6	94.5	100.2	108.0	109.4	116.5	130.4
373.15	79.9	83.4	86.1	91.0	94.0	99.6	107.4	108.8	116.0	129.7
398.15	79.4	83.0	85.7	90.5	93.5	99.1	106.7	108.1	115.4	129.0
423.15	79.0	82.6	85.2	89.9	92.9	98.5	106.1	107.5	115.0	128.4
448.15	78.5	82.2	84.7	89.4	92.4	98.0	105.5	106.9	114.5	127.7
473.15	78.1	81.8	84.3	88.8	91.9	97.5	104.8	106.3	114.0	127.0
498.15	77.6	81.4	83.8	88.3	91.4	97.0	104.2	105.6	113.5	126.4
523.15	77.2	81.0	83.3	87.7	90.8	96.4	103.5	105.0	113.0	125.7

It is clear from Table I that on increasing the temperature the value of Debye θ_D decreases constantly which suggests that this alloy is behaving as liquid more closely to crystalline form at lower temperatures. The reasonable values of θ_D provide additional possibility for these liquids to be in a quasicrystalline state, whereas the value of θ_D increases on increasing the mole concentration of the component having higher molecular weight and vice versa, indicates that on increasing molecular weight the quasicrystalline state is less probable but at lower molecular weight it is more authentic to be stable as in liquid state. It is clear from Table I that on increasing the temperature the value of Debye θ_D decreases constantly which suggests that this alloy is behaving as liquid more closely to crystalline form at lower temperatures. The reasonable values of θ_D provide additional possibility for these liquids to be in a quasicrystalline state, whereas the value of θ_D increases on increasing the mole concentration of the component having higher molecular weight and vice versa, indicates that on increasing molecular weight the quasicrystalline state is less probable but at lower molecular weight it is more authentic to be stable as in liquid state.

Table II. Temperature and composition dependence of Debye temperature (θ_D) for Na-Cs alloy.

T (K)	x=0(Cs)	0.223	0.623	0.703	0.765	0.870	0.907	0.927	0.946	0.958	0.981	1.00
298.15	59	63	74	78	82	95	98	105	117	135	163	219
323.15	59	62	73	78	81	94	97	106	118	135	162	219
348.15	58	62	73	77	81	94	97	107	118	135	161	218
373.15	58	61	72	77	80	94	96	108	119	135	161	217
398.15	58	61	72	76	80	93	96	109	120	135	160	216
423.15	57	60	71	76	80	93	96	109	119	135	160	216
448.15	57	60	71	75	79	93	95	108	119	132	159	215
473.15	56	59	70	75	79	92	95	108	119	132	158	214
498.15	56	59	70	74	78	92	94	108	119	131	158	213
523.15	56	58	70	74	78	92	94	108	118	130	157	213

Table III. Temperature and composition dependence of θ_D for K-Rb alloy

T (K)	w=0(Rb)	0.101	0.190	0.333	0.401	0.528	0.677	0.740	0.897	1.00
298.15	0.00	-1.66	-3.30	-4.91	-5.92	-6.66	-6.14	-7.96	-9.08	0.00
323.15	0.00	-1.16	-3.27	-4.92	-5.90	-6.63	-6.18	-7.97	-8.93	0.00
348.15	0.00	-1.53	-3.25	-4.94	-5.89	-6.59	-6.21	-7.98	-8.79	0.00
373.15	0.00	-1.47	-3.22	-4.96	-5.88	-6.56	-6.25	-7.99	-8.64	0.00
398.15	0.00	-1.40	-3.20	-4.99	-5.86	-6.53	-6.29	-8.01	-8.49	0.00
423.15	0.00	-1.33	-3.17	-5.01	-5.85	-6.49	-6.33	-8.02	-8.34	0.00
448.15	0.00	-1.26	-3.14	-5.03	-5.84	-6.46	-6.37	-8.03	-8.18	0.00
473.15	0.00	-1.19	-3.12	-5.05	-5.82	-6.42	-6.40	-8.04	-8.02	0.00
498.15	0.00	-1.12	-3.09	-5.07	-5.81	-6.39	-6.44	-8.05	-7.86	0.00
523.15	0.00	-1.04	-3.06	-5.09	-5.79	-6.35	-6.48	-8.07	-7.70	0.00

Table IV. Temperature and composition dependence of θ_D for Na-Cs alloy

T (K)	w=0(Cs)	0.223	0.623	0.703	0.765	0.87	0.907	0.927	0.946	0.958	0.981	1.0
298.15	0	-4	-21	-27	-35	-50	-62	-64	-62	-52	-41	0
323.15	0	-4	-21	-27	-35	-50	-62	-62	-61	-51	-40	0
348.15	0	-4	-21	-27	-35	-50	-62	-61	-60	-51	-40	0
373.15	0	-4	-21	-27	-35	-50	-62	-59	-58	-50	-40	0
398.15	0	-4	-21	-27	-35	-49	-61	-58	-57	-49	-40	0
423.15	0	-4	-21	-27	-35	-49	-61	-57	-57	-48	-40	0
448.15	0	-4	-21	-27	-35	-49	-61	-57	-56	-51	-40	0
473.15	0	-5	-21	-27	-35	-49	-61	-57	-56	-51	-40	0
498.15	0	-5	-21	-27	-35	-48	-61	-56	-56	-51	-40	0
523.15	0	-5	-21	-27	-34	-48	-60	-56	-55	-51	-39	0

Table III shows that all the values are negative showing non-ideal behaviour of the liquid alloys. The rise in temperature at each weight fraction shows decreasing trend till 0.528 and reverse till 1.00 mole fraction indicating that on increasing the component with higher molecular weight the θ_D values change abruptly indicating deviation from quasicrystalline state, but with increasing weight fraction more negative values are obtained showing non-ideal behaviour.

The values of $\Delta\theta_D$ have been plotted as w, and shown in Fig. 1 for K-Rb alloys.

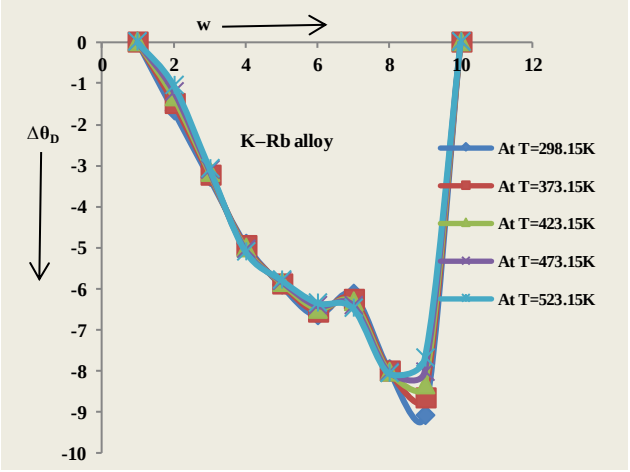

Fig. 1.

Fig. 1 Support the data provided in Table III showing negative trend and deviation from ideal behaviour.

Table IV showing similar trend as in Table III indicating that both alloys behave similarly as they belong to the same block in the periodic table.

The values of $\Delta\theta_D$ have been plotted as w, and shown in Fig. 2 for Na-Cs alloy.

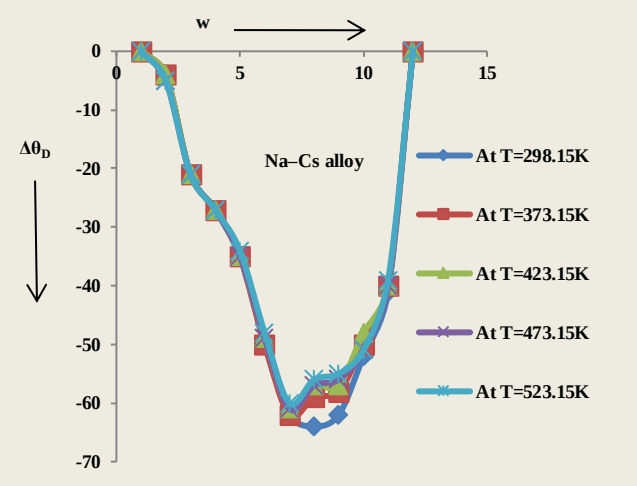

Fig. 2.

Fig. 2 showing more negative behaviour of Na-Cs alloy with change in θ_D confirming that increase in molecular weight of the metals makes the possibility of quasicrystalline structure less probable but is still relevant but for a shorter time range.

It is evident from the results reported in Tables I and II, that for both the alloys the computed values of θ_D decrease with increasing temperature at all the compositions studied. On increasing the amount of first component in each alloy, the values of θ_D increase continuously at all the temperatures .The change in the values of effective Debye temperature with weight fraction, $\Delta\theta_D$, is shown in Table III for K-Rb and Table IV for Na-Cs alloys .The change $\Delta\theta_D$ is found to be negative and increases invariably with increase in temperature for both alloys. The values decrease with increase in composition of first component, minimum at a limiting composition, after which it again increases.

CONCLUSION

The present study of the effective Debye temperature, θ_D, of two liquid metal alloys at different temperatures and varying compositions shows the evidence for the existence of effective Debye temperature, θ_D in liquid metal alloys, assuming their atomic motions similar to those of solids. Treating the alloy as binary liquid mixtures with two liquid metals as components, the θ_D has been calculated and mixing values has been employed to obtained $\Delta\theta_D$, which has been found to be satisfactory on the weight fraction bases.

CONFLICTS OF INTEREST

The authors declare no conflict of interest in the present research work.

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