Journal of Chemical, Biological and Physical Sciences

An International Peer Review E-3 Journal of Sciences

*Available online at*www.jcbsc.org

Section C: Physical Sciences

CODEN (USA): JCBPAT   **Research Article**

Anharmonicity of Lattice Waves in Electronic Specific Heat of Materials at Very Low Temperature

P. Poddar[1], A.K. Sah[2], D.P. Singh[3] & Murari Pd. Sinha[4]

[1]University Department of Physics, Magadh University, Bodh Gaya 824234 (India)

[2]Department of Physics, Birendra Multiple College, Bharotpur, Nepal

[3]P.G. Department of Physics, B.N.M.U. Madhepura (Bihar), India

[4]Department of Physics D.N. College, Masauri (Patna), India

Abstract: In this paper we discuss the role of anharmonicity of lattice waves in electronic specific heat of metals and insulators at very low temperatures. Previous researchers have revealed the anharmonicity of the lattice waves to cause deviation in specific heat from Debye T^3 law. Different researchers have given different concepts of anharmonicity in electronic specific heat of metals at very low temperatures. The energy spectrum of phonons cannot be fully described by the Debye law. On the whole all reports dilute the contention of the electronic contribution to be responsible for linear temperature dependent component of specific heat of metals at very low temperatures. For anharmonicity of lattice waves this contribution must be expected for metals and insulators also.

Keywords: Anharmonicity, Boltzmann's constant, Lattice vibration, Specific heat.

INTRODUCTION

The linear temperature dependent, term in the equation fitting in the data[1-3] Keesom and Kurrelmeyor [4-6] of observed specific heat of metals, Viz, Al, Cu, Ag, Ni, Fe, Pd and Pt was identified with the electronic contribution[7]. It gives a sound support to the free-electron theory of metals[8]. Later experiment [9] revealed the linear term in specific heat of almost all metals, at low temperatures. This linear term differentiates the metals from other elements such as insulators. But intensive study of the transport properties namely thermoelectric properties, thermal and electrical conductivities of metals at low temperatures finds deviation of the electrons from the free electron model at low temperatures. Only in sodium the free electron model is valid in true sense.

In the light of the recent development in this regard the earlier notion of linear temperature dependent term of specific heat appears to be doubtful, because electrons may not contribute independently to specific heat if they are not perfectly free. Very recently several authors[10-29] have revealed the anharmonicity of the lattice waves to cause deviation in specific heat from Debye T^3- law. Debye did not take into account the anharmonicity of the lattice wave in his theory of specific heat of solids at low temperatures, though he admitted the essential presence of anharmonicity of the lattice waves. Since solid expands of heating, the waves are anharmonic and this anharmonicity, according to Debye is the source of coupling between the lattice waves, so that the mutual scatteing of waves is possible. Due to volume expansion the interatomic forces change which results in change of phonon frequency.

 The energy spectrum of phonons cannot be fully described by the Debye law. Naturally Debye T^3- law is not fully obeyed by the observed specific heat of solids. Martin[10] suggests that the contribution to specific heat due to anharmonic effects caused by volume expansion is positive for alkali metals at temperature T<θ/6; θ being the Debye temperature and it is the linear function of temperature. Tosi and Fumi (1963)[30] and Barron *et al.* [31] argued that anharmonic effect must be present from the lowest temperature and its contribution to specific heat is positive and linear function of temperature. Lima[32] also suggests the decrease in the value of θ due to anharmonicity of the lattice vibrations in noble metals. Tolpadi [21] suggests that anharmonicity of lattice waves is caused by two effects, Viz (i) due to volume expansion and (ii) due to phonon-phonon interaction, which change the phonon self-energy. Klemense [33] claims that phonon-phonon interaction is strong enough even at very low temperatures, where volume expansion-anharmonicity is negligible. Lowndes [34] produces the experimental evidence of lattice anharmonicity on the long wave lengths which are at sufficiently low temperatures. On the whole the above reports dilute the contention of the electronic contribution to be responsible for linear temperature dependent component of specific heat of metals at low temperatures. If anharmonicity of lattice waves is also responsible for the contribution to the linear temperature dependent component of specific heat then this contribution must be expected in insulators as well. In this communication, we have analysed the specific heat data of some metals as well as insulators, reported in the literatures, to acertain the contribution of electrons an anharmonicity of lattice waves in metals.

RESULTS AND DISCUSSION

Specific heat of metals and insulators at low temperatures: The specific heat of a metals at low temperatures may be expressed as

$$Cv = \gamma_0 T + BT^3 \tag{1}$$

Where γ_0 is supposed to be the electronic contribution. The conventional free-electron theory of metals give

$$\gamma_0 = (\pi^2 K^2) / (2\mu_o) \tag{2}$$

Where K is the Boltzmann's constant and μ_o is the Fermi energy of electrons at T= 0, BT^3 is the lattice contribution and

$$B = (234R)/\theta^3 \text{ per gram atom} \tag{3}$$

R being the gas constant.

For insulators only the second term in R.H.S. of equation (1) retains we have analysed the specific heat of some metals, Viz. Ba, Ca, Mg, Cu, Ag, Au, Na, K, Cs, Zn and Cd in the low temperature zone These data of specific heat have been taken from the literatures [35]

In the process of analysis we have plotted Cp/T against T^2. The plots are straight line curves. The slope, intercepts of the curves, obtained by least square method, are reported in **Table- 1.** This table also contains correlation factor γ and the temperature zone in which the slope and intercept are valid.

We have also calculated the Debye temperature θ from the slope of the curves **[cf. Table-1** and equation (2)] and values of γ_0 from equation (2). We have used the values of μ_o for the metals under test from the standard text. These values of μ_o are listed in Table-2. The calculated values of γ_0 has been compared with the intercept of the curves and calculated values of θ with that reported in the literatures **[cf. Table-2]**. The sign of γ_0 obtain from the curves is negative in K, Cs, Zn and Cd and positive in Na, Ba, Ca, Mg, Cu, Ag, & Au **[cf. Table-1].** Magnitude of γ_0 obtain from the curves is greater than its theoretical value in almost all cases except in Ag and Au. The deviation between the two values of γ_0 is as large as 95 % in case of Cd, except in Mg, Cd and Zn, in other cases the agreement between the two value of θ is satisfactory. These results show that lattice term i.e. BT^3 is obeyed by the experimental data of specific heat. However, the linear term $\gamma_o T$ is not obeyed. Moreover the negative sign associated with γ_o **[cf. Table-1]** is undesirable. A small deviation in the value of θ from the calculated value may be based on the anharmonic contribution to T^3 term. The anharmonic contribution, if it exists may not be described completely by a few terms of function of temperature. Martin [11] reports equation

$$C_v = \gamma_o T + BT^3 + CT^5 \tag{4}$$

to fit in the data of specific heat of Au, where C is other constant and it is relatively less significant, θ is 345.8 ± 1.2 K, Cetas et al. (1969)[13] report the equation

$C_v = \Sigma\ a_n\ T^n$ $n = 1,3,5,7$ ……………….

$= a_1T + a_3T^3 + a_5\ T^5 +$ …………………………..   (5)

to fit in the data of specific heat of Zn, Cd and Sn in the temperature zone (1-30K). The coefficients 'a$_n$' are constants. The higher order coefficients in equation (5) are generally insignificant. The first two terms dominate over, but the results of the present analysis demands the introduction of some term to the space between first and the second term. We propose equation.

$C_v = a_1T + a_2T^2 + a_3\ T^3 +$ …………………………..   (6)

from specific heat of metals. We have analysed the specific heat data [Touloukian et al. (1970)[35]] of some metals in the light of equation (6). The equations fitting in the data of specific heat, so obtained are written as,

Au : $C_p = 0.17357T + 0.0157354T^2 + 0.0993569\ T^3$ (7)

$(3.49 \leq T \leq 10.07\ K)$

Correlation factor $\gamma = 0.9998$

Ag : $C_p = 0.09725T - 0.0136293T^2 + 0.0431014T^3$ (8)

$(3 \leq T \leq 10\ K\ )$

$\gamma = 0.099934$

Cu : $C_p = 0.1656\ T - 1.36 \times 10^{-3}\ T^2 + 0.01178T^3$ (9)

$(2 \leq T \leq 10\ K)$

$\gamma = 0.9998$

K : $C_p = 0.49523T + 0.2977764T^2 + 0.8429686\ T^3$ (10)

$(1.1 \leq T \leq 4.1\ K)$
$(1.2\ \gamma = 0.997$

Na : $C_p = 0.32856\ T + 0.059\ T^2 + 0.11185T^3$ (11)

$(2 \leq T \leq 20\ K)$

$\gamma = 0.9906$

Ni : $C_p = 1.67143T + 0.0579T^2 + 8.5786 \times 10^{-3}\ T^3$ (12)

$(16.7 \leq T \leq 30.14\ K\ )$

$\gamma = 0.9965$

Pt : $C_p = 1.619\,T - 0.03633T^2 + 0.04094T^3$ (13)

$(2.024 \leq T \leq 20.3\,\text{K})$

$\gamma = 0.998$

Fe : $C_p = 1.1857\,T + 1.037\,T^2 + 3.8337 \times 10^{-3}\,T^3$ (14)

$(4.45 \leq T \leq 20.12\,\text{K})$

$\gamma = 0.988$

Co : $C_p = 1.1262\,T - 0.0646T^2 + 9.528264 \times 10^{-3}\,T^3$ (15)

$(14.3 \leq T \leq 25.7\,\text{K})$

$\gamma = 0.97$

Zn : $C_p = 0.15238\,T + 0.3197T^2 + 0.07T^3$ (16)

$(5.02 \leq T \leq 20.1\,\text{K})$

$\gamma = 0.994$

Al : $C_p = 0.32143T + 7.8509 \times 10^{-3}T^2 + 5.96016 \times 10^{-3}\,T^3$ (17)

$(2.05 \leq T \leq 18.88\,K)$

$\gamma = 0.996$

Pb : $C_p = 0.709524\,T - 0.956T^2 + 0.8403T^3$ (18)

$(2 \leq T \leq 8\,\text{K})$

$\gamma = 0.9855$

The values of a_1 a_2 and a_3 together with the temperature zone in which the constants are valid, are summarised in Table-3. We have also calculated the value of θ from equation (3) using a_3 of **Table- 3**.

These values of θ are also shown in the same **Table- 3**. These values of θ lies in the neighbourhood of their values reported in the literatures. A unique value of θ for a metal cannot be taken because different sources [Elastic constants, Thermal and Electrical Conductivities] give varying value of θ. Ultimately we have come to the conclusion that the specific heat of a metal may be well represented by the equation of the form,

$C_v = \Sigma\,a_n\,T^n$ (19)

Where n = 1, 2, 3, 4, 5, …………………………

Thus either equation (1) or equation (5) does not give the true picture of the temperature variation of specific heat of metals. Equation (19) is supposed to be of more convenient form than the earlier ones [cf.

equation (1) & (5)] because equation (19) preserves the contention of positive contribution of either electrons or anharmonic lattice waves to specific heat whereas equation (1) does not do [**cf. Table- 1].**

In fact anharmonicity of lattice waves may lead to complicated temperature variation of C_v of metals. Though we have analysed the data of C_p and describe the property of C_v. It is not unjustified because at very low temperatures anharmonicity due to volume expansion is negligible and that due to phonon-phonon interaction dominates. Therefore, we may take $C_p = C_v$ for all practical purposes.
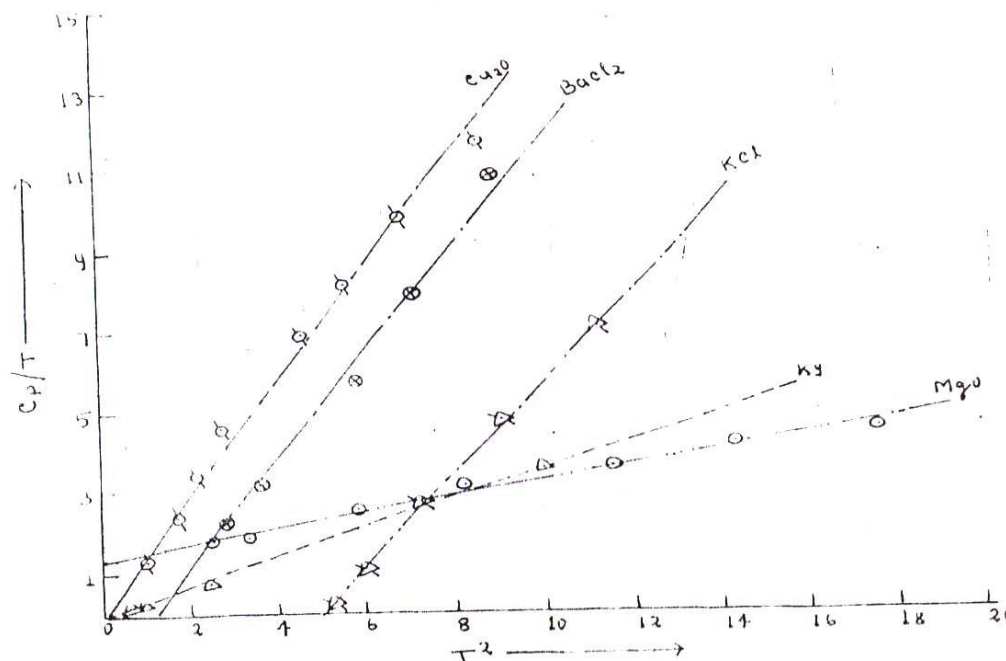

Fig. 1: Plots between C_p/T and T^2 of insulators [The scales and origin have been suitably altered to portray the desired shape of the curves].

The above discussion and result identify the linear temperature dependent term with the contribution of anharmonicity of lattice waves rather than the electrons in the specific heat of metals. To confirm this contention we have analysed the specific heat data [34] of some insulators viz. KI, KCl, Mgo, Bacl$_2$ and Cu$_2$o. We have plotted Cp/T against T^2 [**Figure (1)].** The plots are straight lines. The slope, intercept and correlation factor of the curves obtained by least square method are listed in Table-4. The equation (1) is well obeyed by the specific heat of these insulators. The intercept is positive in KCl, Mgo, Bacl$_2$ and Cu$_2$o and negative in KI. **[cf. Table-4].**

Table -1: Results of the analysis of the specific heat (Cp) of some metals in the low temperature region. The slope, intercept and γ are obtained by least square method.

Metals	Correlation factor (γ) (JKg^{-1} K^{-2})	Slope × 10^{-5}	Intercept ×10^{-5} (γ_o)	Temp. Zone (in K)
Na	0.9997	0.559	0.8784	$1.5 \leq T \leq 10.0$
K	0.9994	2.1017	-0.5037	$1.697 \leq T \leq 4.10$
Cs	0.9991	7.5917	-0.8824	$1.2031 \leq T \leq 2.45$
Mg	0.9918	0.0337	1.1979	$3.14 \leq T \leq 9.71$
Ca	0.9998	0.0982	1.6167	$1.5 \leq T \leq 5.0$
Ba	0.9978	0.2862	0.2462	$1.5 \leq T \leq 5.0$
Zn	0.9999	0.0704	-1.6082	$7.07 \leq T \leq 10.20$
Cd	0.9996	0.2403	-2.7295	$4 \leq T \leq 10.0$
Cu	0.9904	0.0182	0.2614	$1.5 \leq T \leq 10.0$
Ag	0.9997	0.0393	0.0902	$3 \leq T \leq 10.0$
Au	0.9999	0.0506	0.1069	$3.49 \leq T \leq 9.25$

Table -2 : Values of θ [Thermo-physical properties of matter (1970)[35]]. Values of θ calculated from equation (3). The observed value of γ_o was taken from curve and the calculated values of γ_o was calculated from equation (2) values of μo [Introduction of solid state physics. Fifth edn. By C. Kittel[36]]

Metals	θ calculated in the present study	θ Reported in the literatures	γ_o(observed) from graph in J×10^{-3}	μo (Fermi energy) in ev	γ_o(Calculated) Theoretically in J×10^{-3}	Difference of $\gamma_o$observed in ×10^{-3}	Percentage error %
Na	154.586	157±1	1.442	3.23	1.096	0.346	24
K	82.323	89.4±0.5	-1.634	2.12	1.670	0.036	2
Cs	35.916	40 ± 5	-4.166	1.58	2.240	1.925	46
Mg	365.370	396 ± 54	0.863	7.13	0.497	0.367	43
Ca	230.311	234 ± 5	2.759	4.68	0.756	2.002	72
Ba	108.91	110.5 ± 18	2.577	3.65	0.970	1.607	62
Zn	216.141	316 ±20	-4.372	9.39	0.377	3.995	91
Cd	119.924	254 ± 48	-11.746	7.46	0.475	11.271	95
Cu	346.682	342 ±2	0.664	7.00	0.506	0.158	24
Ag	221.545	228 ± 3	0.451	5.48	0.646	0.195	43
Au	166.123	165 ± 1	0.477	5.51	0.643	0.165	34.5

Table – 3 : Values of a_1[Lien & Phillips (1964)[9]]. Values of a_2 & a_3 calculated from eqn. (6) values of Cp [Thermo-physical properties of matter (1970)[35]]. Values of θ calculated from the coefficients of T^3 ie. B [cf. eqn. (3)].

Metals	$a_1(\times 10^3)$ JKg^{-1} K^{-2}	$a_2(\times 10^5)$ JKg^{-1} K^{-3}	$a_3(\times 10^5)$ JKg^{-1} K^{-4}	Temp. Zone	θ K
Au	0.17357	1.57354	9.93569	3.49-10.07	168.07
Ag	0.09725	-1.36293	4.31014	3-10	220.86
Cu	0.1655	-0.136	1.17802	2-10	340.08
K	0.49523	29.77764	84.29686	1.1-4.1	81.92
Na	0.32856	5.91176	11.18473	2-20	160.6
Ni	1.67143	5.79085	0.85786	16.7-30.14	378
Pt	1.619	-3.63254	4.09368	2.024-20.3	224.5
Fe	1.1857	1.03701	0.38337	4.45-20.12	494.4
Co	1.12619	-6.4601	0.95263	14.27-25.73	365
Zn	0.15238	31.97107	6.99387	5.02-20.1	187.8
Al	0.32143	0.785092	0.596016	2.05-18.9	426.8
Pb	0.709524	-95.60416	84.07954	2-8	81.98

Table- 4: Results of the analysis of the specific heat (C_p) of some insulators in the low temperature region. The slope, intercept and γ are obtained by the least square method.

Insulators	Correlation factor (γ) JKg^{-1} K^{-2}	Slope $\times 10^{-5}$	Intercept $\times 10^{-5}$ (γ_0)	Temp. Zone (inK)
Kcl	0.9988503	0.113921	0.0956723	$2.5 \leq T \leq 25$
KI	0.9996966	0.3571986	-1.036728	$2.5 \leq T \leq 10$
Mgo	0.9945082	0.0193514	0.1271317	$1.612 \leq T \leq 4.12$
BaCl$_2$	0.9952367	0.1412052	2.1117103	$5.36 \leq T \leq 9.44$
Cu$_2$O	0.9967434	0.1361717	0.3555968	$3.087 \leq T \leq 9.27$

The order of the magnitude of the intercept in case of insulators is the same as it is in metals [cf. Table 1 & 4]. Equation (19) may be expected to be obeyed by the specific heat of insulators also. The Table-4 gives clear-cut evidence of the contribution of anharmonicity of lattice waves at very low temperatures from the lowest temperature. These results confirm the contention of Tosi and Fumi (1963)[30]; Barron (1967)[31]and Klemense (1951)[33]. Since in an insulators the possibility of electronic contribution can be totally ruled out. Therefore, the linear temperature component of specific heat of metals, may not be solely due to electrons, Tosi and Fumi (1963)[30] and Barron (1967)[31] suggests

Cv-(Cv)$_{har}$ = 3NKT   (20)

This equation also imphasises on the contribution of anharmonicity of lattice waves.

CONCLUSION

On the basis of the results of the analysis of the specific heat of metals and insulators it may be concluded that the linear temperature dependent component of specific heat of metals at low temperatures is due to the anharmonicity of lattice waves rather than the electrons. Other deviation from the Debye T^3 law may also be based on the anharmonicity of lattice waves from the lowest temperature.

REFERENCES

1. W.H. Keesom & J.A. KoK, *Physica*, 1934, 1, 770

2. W.H. Keesom & J.A. KoK, *Physica*, 1936, 3, 1035.

3. W.H. Keesom & J.A. KoK, *Physica*, 1937, 4, 835.

4. W.H. Keesom & B. Kurrelmeyer, *Physica*, 1939, 6, 364.

5. W.H. Keesom & C.M. Clark, *Physica*, 1935, 2, 513.

6. G.L. Pickard, *Nature (*London*)*, 1936, 138, 123.

7. Sommerfeld, *Z. Phys,* 1928, 47, 1.

8. P. Drude, *Ann. Phys. LPZ*(4), 1900, 1, 566.

9. W.H. Lien & N.E. Phillips, *Phys. Rev*., 1964, 133, A1370.

10. D.L. Martin*, Phys. Rev*. 1965, 138, A434.

11. D.L. Martin, *Rev. Sci. Inst*. 1967, 38, 1738.

12. Cetas *et al., Phys. Rev*., 1979, 151, 181.

13. Cetas et al., *Phys. Rev*., 1969, 151, 2679.

14. W.T. Berg, *Phys Rev*. 1968, 167, 583.

15. H.C. Gupta & B.B. Tripathi, *I.J. Phys. Appl. Phys*., 1971, 9, 1034.

16. D.R. Chipman, *J. Appl. Phys*., 1960, 31, 2012.

17. F.H. Herbstein, *Adv. Phys.,* 1961, 10, 313.

18. Paskin, *Acta. Cryst*., 1957, 10, 667.

19. R.F. Dingle et al., *Acta. Cryst*. 1972, 28A, 22.

20. S. Tolpadi, *I.J.P.A.P*. 1975, 13, 503.

21. S. Tolpadi, *Physica*, 1975, 79, 21.

22. S. Tolpadi, *Ind. J. Physics*, 1977, 51A, 173.

23. P. Poddar, *Acta Ciencia Indica*, 1992, 4, 257.

24. P. Poddar & J.P. Choudhary, *Acta Ciencia Indica*, 1995, 4, 99.

25. Sanjay Kumar *et al,*. *J. Pure Appl & Ind. Phys*., 2013, 3(2), 88.

26. Purushottam Poddar, *J. Chem. Bio. Phy. Sci. Sec. A*, 2015, 5, 1728.

27. P. Poddar & Shekhar, *IRJET*, 2015, 2, 1115.

28. P. Poddar and Shekhar, *J. Pure Appl & Ind. Phys*. 2017, 7 (8), 335.

29. P. Poddar and Murari Prasad Sinha, *IOSR J. Appl. Phys*., 2017, 4, 01.

30. M.R. Tosi & F.G. Fumi, *Phys. Rev*. 1963, 131, 1458.

31. T.H.K. Barron & R.W. Mann, *Phil. Mag*, 1967, 15, 85.

32. R.A.T. Lima, *Phys. Rev.* 1980, B 31, 458.

33. P.G. Klemense, *Proc. Phys, Soc*. 1951, A64, 1030.

34. R.I. Lawndes, *Thermo Physical Properties of Matter*, 1972, 4.

35. Touloukian et al., *Thermo Physical Properties of Matter*, 1970. Plenum Pub. Corp. N.Y.4.

36. C. Kittel, *Introduction to Solid State Physics*, 1977, Willey Eastern Pvt. Ltd.

* Corresponding author: Dr. P. Poddar,

University, Department of Physics, Magadh University, BodhGaya-824234 (India)

Online publication Date: 28.03.2018