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Specific heat jump and transition temperature T_C for $La_{2-x}Ba_xCuO_4$, $Bi_2Ca_{n-1}Sr_nCu_nO_{2n+3}$ and $Tl_2Ca_{n-1}Ba_2Cu_nO_{2n+3(2n+4)}$ superconductors

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The transition temperature T_C and the specific heat jump $\Delta C/T_C$ in $La_{2-x}Ba_xCuO_4$, $Bi_2Ca_{n-1}Sr_nCu_nO_{2n+4}$ and $Tl_2Ca_{n-1}Ba_2Cu_nO_{2n+3(2n+4)}$ are calculated using exotic pairing model. These values are calculated at both buckling mode and breathing mode. The values calculated are compared with known experimental values. If Δ is the gap in the allowed energy states, then the jump in the specific heat is $C_S - C_n$. These results show that the calculated values of the ratios and T_C compare well with experimental values.

Keywords: Specific heat, Superconductors, Density of states

1 Introduction

The bulk properties of solids, primarily integral characteristics of the excitation spectrum of electronic, phononic and magnetic degrees of freedom[1] have been investigated by knowledge of specific heat. In particular, the observation of the specific heat jump occurring at the superconducting phase transition in oxide superconductors has confirmed the bulk nature of high temperature superconductivity. The specific heat of YBCO and LMCO has been best studied, while that of Bi and Tl compounds has been studied less[3-7].

The parent compound of the La-Ba-Cu-O superconductor, La_2CuO_4, is anti-ferromagnetic insulator. The CuO planes in this case do not have any metallic characteristics. As Ba, Sr or Ca are added to the compound, electrons are removed from the CuO plane leaving behind vacancies (holes) in the band. Eventually, there are enough holes to make the CuO layers metallic and superconducting.

$Bi_2Ca_{n-1}Sr_nCu_nO_{2n+4}$ is a bismuth based superconductor where n = 1, 2, 3 are the number of immediately adjacent CuO planes. The higher the number of CuO planes, the higher the transition temperature up to saturation[1]. This compound has n immediately adjacent CuO planes with a calcium plane in between Sr-O and two Bi-O planes which separate these immediately adjacent planes before the next Cu-O plane. Its high-T_C is attributed to long periodic modulated superstructure in x-y plane, existence of several closely related structures of Sr and Bi-O and stabilized modified perovskite structure. The compounds $Tl_2Ca_{n-1}Ba_2Cu_nO_{2n+3(2n+4)}$ and $Tl_2Ca_{n-1}Ba_2Cu_nO_{2n+3(2n+3)}$ contain n immediately adjacent Cu-planes with a Ca plane between each immediately adjacent Cu-O plane[2].

The planes Ba-O, Tl-O and another Ba-O separate these CuO planes. This compound has three different types of oxygen atoms that is O_p oxygen atoms in the Cu-O plane, O_z apical oxygen atoms directly above and is part of Ba-O plane and O_{oct} oxygen atoms that are part of planes and in octahedral surrounded by Tl and Ba atoms. The existence of several equivalent positions of oxygen atoms causes a strong anharmonic perturbation, which can increase the electron-phonon coupling[4,5] leading to increase in transition temperature T_C. Specific heat discontinuity ΔC at T_C due to the second order transition of the normal state to superconducting state and the electronic specific heat coefficient γ (Sommerfeld gamma) are important properties of all these three superconducting materials. This specific heat coefficient is proportional to the density of electronic states at the Fermi surface and is one of the parameters which specify the interactions of the electrons and hence, used to determine the transition temperature T_C. The knowledge of these electronic properties may lead to understanding of high T_C mechanisms.

Exotic pairing[5] has been reported to be contributing to high T_C in $YBa_2Cu_3O_{7-\delta}$. Applying the same to

$La_{2-x}Ba_xCuO_4$, $Bi_2Ca_{n-1}Sr_nCu_nO_{2n+4}$ and $Tl_2Ca_{n-1}Ba_2Cu_nO_{2n+3(2n+4)}$ shows that anharmonic perturbation of phonons with quadratic temperature dependence significantly increases the transition temperature. The shapes of the specific heat graphs for superconducting phase C_S and normal phase C_n as function of temperature[8] indicate shape of specific heat jumps typical of superconducting state giving support to exotic pairing theory due to anharmonic perturbation as contributing to the electron-phonon coupling. The graphs are linear for C_n but for C_S it has two sections. First, is an exponential term for $0 \le T \le 0.7T_C$ indicating existence of energy gap in the electronic energy levels and secondly, the linear term for $0.7T_C \le T \le T_C$. This is a further proof that the properties of the specific heat discontinuities and the specific heat coefficient and their dependence on the T_C may be essential to understand the nature of superconducting transition in high-T_C ceramic oxides. In normal state, the specific heat is composed of the lattice contribution and the electronic contribution given as $C_n = C_1T + C_2T^3$ where C_2T^3 is associated with Debye vibrations of lattice. At very low temperatures, the linear term C_1T dominates which arises from the kinetic energy of the heat motions of the electron gas in the superconducting state. The phonon specific heat $C_{es} \alpha \exp(-\Delta/T)$ dominates at low temperatures and vanishes exponentially in the limit of very low temperatures. In superconducting state $C_S = 3\gamma T^2/T^3_C$ where $3\gamma/T^2_C$ is the gradient of the linear part of the curve.

At very low temperature, phonon contribution will be negligible in superconducting state and the specific heat will be due to the electronic motion. In YBCO, the ratio C_S/C_n is 2.43 at $T = T_C$ where C_S is the specific heat in the superconducting state and C_n is specific heat in the normal state. The specific heat jump is the sudden rise in specific heat at transition temperature when specific heat values are plotted against temperature. In this paper, the transition temperature T_C and specific heat jump ΔC are calculated.

2 Theory

The well known BCS theory is not able to explain the properties of high-T_C superconductors. However, pairing of electrons does occur and the said pairing is assumed to be exotic[5]. In this theory, it is assumed that there are three electrons that take part in superconducting current and these electrons interact with each other through harmonic forces. Two of these electrons form a bound pair while the third one is a polarization electron which hops from one lattice site to another site of similar symmetry. Photo-induced Raman scattering studies have confirmed that there exists strong anharmonic nature of apical oxygen vibrations[1]. In fact, when spectral function of electron-phonon interactions is compared with phonon spectrum in bismuth compounds, it shows that both low frequency vibrations (buckling mode) and high frequency vibrations (breathing mode) contribute to the electron-phonon coupling[6]. Thus, polarization electron causes perturbation with respect to apical oxygen vibrations leading to contraction of Cu_p-O_z bond. This perturbation is of the form:

$$\beta x^3 + \gamma x^4 \qquad \ldots(1)$$

where β and γ are perturbation parameters. At low temperatures, the phonon contribution to specific heat is :

$$C_n = C_1T + C_2T^3 \qquad \ldots(2)$$

When phonon contribution is neglected, then the term C_2T^3 does not contribute to the specific heat. Eq. (2) becomes:

$$C_n = \gamma T \qquad \ldots(3)$$

where γ replaces C_1 and is the specific heat coefficient (Sommerfeld gamma). In superconducting state, the specific heat is:

$$C_S = \frac{3\gamma T^3}{T_C} \qquad \ldots(4)$$

which can be assumed to be of the form $C_S \alpha \exp(-\Delta/kT)$ before the heat jump because of the existence of the energy gap in the temperature range $0 \le T \le 0.7T_C$. If the specific heat jump is $\Delta C/T_C$ then at $T = T_C$, $C_n = \gamma T_C$

$$\frac{\Delta C}{T_C} = \frac{C_S - C_n}{T_C} = C_n\left(\frac{C_S}{C_n} - 1\right)\frac{1}{T_C} \qquad \ldots(5)$$

at $T = T_C$; $C_n = \gamma T_C$.
Thus, Eq. (5) is:

$$\frac{\Delta C}{T_C} = \gamma T_C\left(\frac{C_S}{C_n} - 1\right)\frac{1}{T_C}$$

Hence

$$\frac{\Delta C}{T_C} = \gamma\left(\frac{C_S}{C_n} - 1\right) \qquad \ldots(6)$$

where $\Delta C = C_S - C_n$ is the specific heat jump. The perturbation is of the form of Eq. (1) and constants γ and β represent the asymmetry of the mutual repulsion of the atoms and softening of the vibrations at large amplitudes, respectively. They may or may not be temperature dependent. The eigenvalues and eigenfunctions of the unperturbed harmonic oscillator are determined from Hamiltonian H_0 given as:

$$H_0 \mid n_1 >= E_n^0 \mid n, 0 > \qquad \ldots(7)$$

When the system is perturbed then Eq. (7) becomes:

$$H \mid n >= (H_0 + H^1) \mid n > E_n^0 \mid n, 0 > \qquad \ldots(8)$$

where $H^1 = \beta x^3 + \gamma x^4$. The total energy of the system[4] is of the form:

$$\varepsilon_n = \left\{\left(n + \frac{1}{2}\right)\hbar\omega + \frac{3\gamma\hbar^2}{2\mu^2\omega^2}\left(n^2 + n + \frac{1}{2}\right) - \frac{15\hbar^2}{\beta^2}4\mu^3\omega^4\left(n^2 + n + \frac{11}{30}\right)\right\}\exp^{-\frac{\Delta E}{kT}}$$

$$= A_1 + \left(A_2\gamma + A_3\beta^2\right)\exp^{-\frac{\theta}{T}} \qquad \ldots(9)$$

where $A_1 = \left(n + \frac{1}{2}\right)\hbar\omega, A_2 = \frac{3\gamma\hbar^2}{2\mu^2\omega^2}\left(n^2 + n + \frac{1}{2}\right)$, $A_3 = \frac{15\hbar^2}{\beta^2}4\mu^3\omega^4\left(n^2 + n + \frac{11}{30}\right)$ and $\theta = -\frac{\Delta E}{k}$.

The specific heat $C = \frac{\partial \varepsilon_n}{\partial T}$. Now, three cases arise depending upon how β and γ depend on the temperature.

(1) β and γ are linear functions of temperature; (2) β and γ are quadratic functions of temperature; (3) β and γ are independent of temperature.

In this work, we assume that β and γ are quadratic functions of temperature. The calculations are done for both buckling modes which are perturbations that occur at low temperature 580 K and breathing modes are calculated at high temperatures of 1160 K. The parameters β and γ are defined as:

$$\beta = \frac{k^2T^2}{a_o^3\hbar\omega}, \ \gamma = \frac{kT}{a_o^4\hbar\omega} \qquad \ldots(10)$$

From Eq. (8), energy ε_n can be expressed as:

$$\varepsilon_n = A_1 + (A_rT^2 + A_ST^4)\exp^{-\frac{\theta}{T}} \qquad \ldots(11)$$

where $A_r = \frac{A_2k^2}{a_o^4\hbar\omega}$, $A_S = \frac{A_3k^4}{a_o^6\hbar^2\omega^2}$ and

$$C = \left\{A_r\theta + 2A_rT + A_S\theta T^2 + 4A_ST^3\right\}\exp^{-\frac{\theta}{T}} \qquad \ldots(12)$$

3 Results

3.1 Breathing Mode

(i) $La_2Ba_2Cu_2O_4$

From Ref. (8) and Eq. (12), the expression for specific heat is found to be:

$$C = \exp^{-\frac{1160}{T}}\{8.91\times10^{-21} + 1.54\times10^{-23}T - 2.02\times10^{-25}T^2 - 1.74\times10^{-28}T^3\} \qquad \ldots(13)$$

Figure 1 shows the variation of specific heat versus temperature. The value of T_C is read from the graph at the point coinciding with the linear graph. Volume of states $V(O)$ is determined as in Ref. [7]. When the C_S curve and C_n are compared at the specific heat jump, the specific heat coefficient $\gamma = 3.0\times10^{-26}$ J/K. From Eq. (5), the specific heat jump and other ratios can easily be determined. Here $C_n = 5.84\times10^{-24}$ JK^{-1} and $T_C = 194$ K.

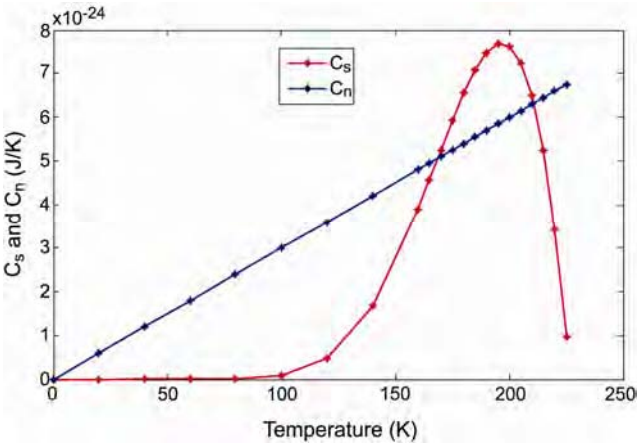

Fig. 1 — C_s and C_n versus temperature for La (n=1)

$$\frac{\Delta C}{C_n}=\frac{\Delta C}{\gamma T_C}=0.313, \gamma=\frac{C_n}{T_C}=18.12\ \text{mJK}^{-2}\text{mol}^{-1}$$
$$=1.812\ \text{mJK}^{-2}g-at.^{-1}$$

V(O)(states/ev.atom)=3.75(states/ev.Cu.atom),

$$\frac{C_S}{C_n}=1.31$$

Specific heat jump is then given as:

$$\frac{\Delta C}{T_C}=1.83\gamma=5.673\ \text{mJK}^{-2}\text{mol}^{-1}$$

(ii) $Bi_2Ca_{n-1}Sr_nCu_nO_{2n+4}$

In Ref. (8), the specific heat for breathing mode for the compound $Bi_2Ca_{n-1}Sr_nCu_nO_{2n+4}$ is given as:

$$C=\exp^{-\frac{1160}{T}}\{4.34\times10^{-22}+7.48\times10^{-25}T$$
$$-2.17\times10^{-27}T^2-7.48\times10^{-30}T^3\}\quad\ldots(14)$$

Again at jump (Fig. 2), the values for transition temperature, specific heats and specific heat coefficient γ can be obtained. C_n = 1.89×10^{-24} J/K, C_S = 5.5×10^{-24} J/K and T_C = 322 K.

$$\frac{\Delta C}{C_n}=\frac{\Delta C}{\gamma T_C}=1.91\gamma=\frac{C_n}{T_C}=3.53\ \text{mJK}^{-2}\text{mol}^{-1}$$
$$=0.176\ \text{mJK}^{-2}g-at.^{-1}$$

V(O)(states/ev.atom)=0.487(states/ev.Cu.atom), (C_S/C_n)=2.91 and the specific heat jump is 6.75 mJK^{-2}mol^{-1}.

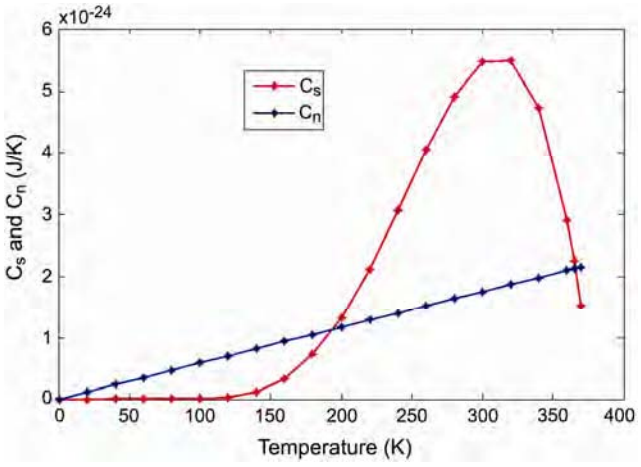

Fig. 2 — C_s and C_n versus temperature for Bi (*n*=3)

(iii) Tl (*n*=3) $Tl_2CaBa_2(CuO_3)_3$

Specific heat equation for Tl (*n*=3) for the breathing mode is here derived as found in Ref. (8). Fig. 3 shows the variations of specific heat with temperature.

$$C=\exp^{-\frac{1160}{T}}\{4.01\times10^{-22}+6.92\times10^{-25}T$$
$$-1.94\times10^{-27}T^2-6.68\times10^{-30}T^3\}\quad\ldots(15)$$

C_n = 1.94×10^{-24}JK^{-1}, C_S = 5.5×10^{-24} JK^{-1} and T_C = 322 K

$$\frac{\Delta C}{C_n}=\frac{\Delta C}{\gamma T_C}=1.83\gamma=\frac{C_n}{T_C}=3.64\ \text{mJK}^{-2}\text{mol}^{-1}$$
$$=0.214\ \text{mJK}^{-2}g-at.^{-1}$$

$V(O)$(*states/ev.atom*) = 0.502(*states/ev.Cu.atom*), C_S/C_n=283. Then, specific heat jump is 6.66 mJK^{-2}mol^{-1}.

3.2 Buckling Mode

3.2.1 La (n=1) $La_2Ba_2Cu_2O_4$

Specific heat equation for superconducting phase is obtained from the Eq. (16):

$$C=\exp^{-\frac{580}{T}}\{3.56\times10^{-20}+1.23\times10^{-22}T$$
$$-6.49\times10^{-47}T^2-4.48\times10^{-26}T^3\}\quad\ldots(16)$$

Fig. 4 is used to get the relevant values.

C_n = 3.156×10^{-25} JK^{-1}, C_S = 6.579×10^{-25} JK^{-1} and T_C = 62 K.

$$\frac{\Delta C}{C_n}=\frac{\Delta C}{\gamma T_C}=1.085\gamma=\frac{C_n}{T_C}=3.06\ \text{mJK}^{-2}\text{mol}^{-1}$$
$$=0.214\ \text{mJK}^{-2}g-at.^{-1}$$

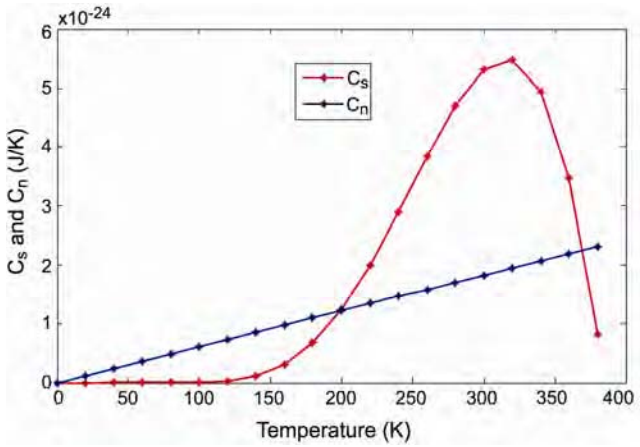

Fig. 3 — C_s and C_n versus temperature for Tl (*n*=3)

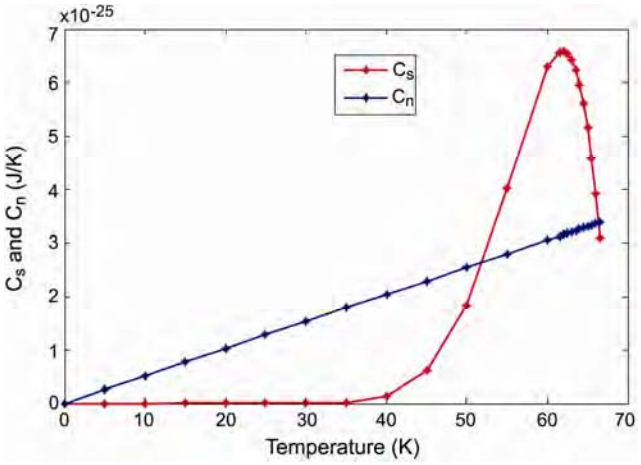

Fig. 4 — C_s and C_n versus temperature for buckling mode for La (n=1)

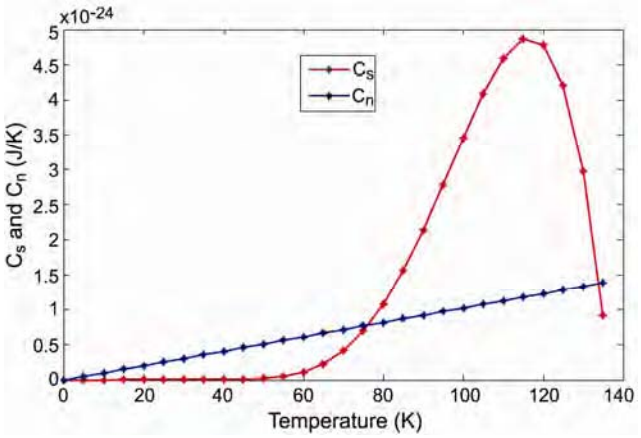

Fig. 5 — C_s and C_n versus temperature for buckling mode for 2Bi(n=3)

$V(O)(states/ev.atom)$ = $0.634(states/ev.Cu.atom)$, C_S/C_n=2.085. The specific heat jump is 3.32 $mJK^{-2}mol^{-1}$

3.2.2: 2Bi (n = 3) $Bi_2Ca_2Sr_3Cu_3O_{10}$

The superconducting phase of 2Bi (n = 3) for its buckling mode state is given in Eq. (17):

$$C = \exp^{-\frac{580}{T}}\{1.73\times10^{-21} + 5.98\times10^{-24}T - 7.02\times10^{-26}T^2 - 4.48\times10^{-28}T^3\} \quad \ldots(17)$$

From Fig. (5), C_S = 4.86×10^{-24} JK^{-1}, C_n = 1.207×10^{-24} JK^{-1} and T_C = 115 K.

$$\frac{\Delta C}{C_n} = \frac{\Delta C}{\gamma T_C} = 3.03\gamma = \frac{C_n}{T_C} = 0.332 \text{ mJK}^{-2}\text{mol}^{-1} = 6.31 \text{ mJK}^{-2} g-at.^{-1}$$

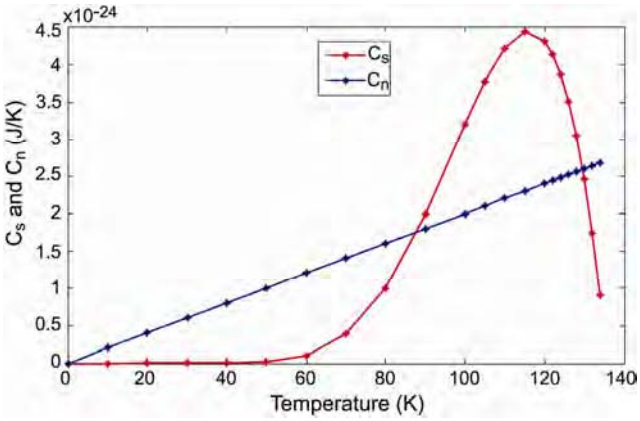

Fig. 6 — C_s and C_n versus temperature for buckling mode of 2Tl (n=3)

Table 1 — Summary of results

	$\Delta C/C_n$	γ ($mJK^{-2}g$–at)	V(O) (states/ ev.Cu.atom)	C_S/C_n	$\Delta C/T_C$
1. $La_2Ba_2Cu_2O_4$	0.313	1.812	3.750	1.31	5.672
2. $Bi_2Ca_{n-1}Sr_nCu_nO_{2n+4}$	1.91	0.176	0.487	2.91	6.750
3. $Tl_2CaBa_2(CuO_3)_3$	1.83	0.214	0.502	2.83	6.660
4. $La_{2-x}Ba_xCuO_4$	1.085	0.306	1.267	2.09	3.320
5.$Bi_2Ca_{n-1}Sr_nCu_nO_{2n+4+}$	3.03	0.332	0.871	4.02	19.12
6.$Tl_2CaBa_2(CuO_3)_3$	1.083	0.668	1.661	2.08	13.03

$V(O)(states/ev.atom)$ = $0.871(states/ev.Cu.atom)$, $\frac{C_S}{C_n} = 4.02$

Hence, specific heat jump $= \frac{\Delta C}{T_C} = 19.12$ $mJK^{-2}mol^{-1}$.

3.2.3: 2Tl (n = 3) $Tl_2Ca_2Ba_2(CuO_3)_3$

Eq. (18) is the derived equation for the superconducting specific heat for 2Tl (n = 3) for buckling mode:

$$C = \exp^{-\frac{580}{T}}\{1.61\times10^{-21} + 5.54\times10^{-24}T - 6.26\times10^{-26}T^2 - 4.82\times10^{-28}T^3\} \quad \ldots(18)$$

From Fig. (6), C_S = 5.0×10^{-24} JK^{-1}, C_n = $2.4\times10^{-24}JK^{-1}$ and T_C = 119.8 K.

$$\frac{\Delta C}{C_n} = \frac{\Delta C}{\gamma T_C} = 1.083\gamma = \frac{C_n}{T_C} = 12.04 \text{ mJK}^{-2}\text{mol}^{-1} = 0.668 \text{ mJK}^{-2} g-at.^{-1}$$

$V(O)(states/ev.atom)$ = $1.6611(states/ev.Cu.atom)$, $\frac{C_S}{C_n} = 2.08$.

Specific heat jump is 13.03 $mJK^{-2}mol^{-1}$.

4 Discussion

Table 1 presents the summary of the calculations. The electronic specific heat[9] decreases exponentially at temperature $T<T_C$ and vanishes at $T<<T_C$ without any residual specific heat. This characteristic is displayed in both low and high frequency modes.

From the present study, it is clear that only $La_2Ba_2Cu_2O_4$ has the highest density of state of 3.75, the rest of the compounds have lower density of states compared to as given in Ref. (7). This low density of states[9] indicates few paired carriers close to the Fermi surface in the CuO planes. $La_2Ba_2Cu_2O_4$ has density of states within the experimental values of YBCO. This may be as a result of two Cu carriers instead of three in YBCO. In BCS theory, specific heat jump A=1.43. For three compounds, we have $0.313<A<1.91$. Large A is associated to strong coupling via high frequency phonons and $A<1$ is low frequency modes of vibration. It can then be concluded that these compounds have both high and low modes of vibrations. Transition temperature T_C is proportional to either buckling mode or breathing mode. High T_C corresponds to high frequency mode of vibration.

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