Specific Heat and Entropy of a Three Electron Model in Bismuth Based Cuprate Superconductor

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Abstract: A theoretical study considering Bi2201, Bi2212 and Bi2223 bismuth based cuprates whose critical Temperatures (T_C) are 20K, 95K and 110K with one, two and three CuO_2 planes respectively; based on a three electron model in Bismuth based cuprates oxide shows that there is a direct correlation between energy of interaction and the number of CuO_2 planes at the T_C. The specific heat for a mole of Bismuth based cuprates at T_C was found to be 7.471×10^{-24} JK^{-1} regardless of the number of CuO_2 planes; though the specific heat per unit mass, Sommerfeld coefficient as well as entropy per unit mass decreased with an increase in the number of CuO_2 planes. The entropy of a mole of Bismuth based cuprates at T_C was found to be 5.603×10^{-24} JK^{-1} irrespective of the T_C or mass. The peak Sommerfeld coefficient temperature was noted to occur at the ratio $T/T_C = 0.66$ in the bismuth based cuprates.

Keywords: Superconductivity, Sommerfeld Coefficient, Specific Heat, Entropy

1. Introduction

Cuprate superconductivity has been studied for the past three decades due to the foreseen applications that will revolutionize the world if the microscopic mechanism behind high temperature superconductivity is discovered. Superconductivity was first discovered by Kamerligh Onnes in 1911 [1], and a further discovery of High Temperature superconductivity (HTS) by Bednorz and Mueller in 1986 [2] inspired intensive research in this area of cuprate high temperature superconductivity resulting to the discovery of Y-Ba-Cu-O [3], Bi-Sr-Ca-Cu-O [4], Tl-Ba-Ca-Cu-O [5] and Hg-Ba-Ca-Cu-O [6]. The highest achieved experimental critical temperature (T_C) is 140 K in optimally oxygen doped mercury cuprates superconductor $HgBa_2Ca_2Cu_3O_x$ at ambient pressure [7] and 156 K under 2.5×10^{10} Pa pressures in the same substance [8]. Iron based HTS was discovered in 2008 [9], whereas in 2015 the highest experimental T_C of 203 K under pressures of 200 GPa was found in a non – cuprate Sulfur Hydride (H_2S) [10].

The discovery of Bismuth based superconductor was first done by Michel *et al.*, in 1987 [11]. The T_C for this bismuth based cuprates ranged between 7 and 22 K containing Bi-Sr-Cu-O. This discovery was overshadowed by the nearly immediate discovery of $YBa_2Cu_3O_{7-\delta}$ which achieved a T_C of 93 K [3]. However in January 1988, Maeda *et al.*, reported a new compound of bismuth based cuprates after adding calcium to the initial compound used by Michel *et al.*, and achieving a T_C of about 110 K [4]. This encouraged researcher in this area to focus on bismuth based compound because the material's T_C was above liquid nitrogen boiling point, an indication that nitrogen can be used as a cryogenic material rather than the expensive mercury. Bismuth based HTS cuprate compounds can be described by the general formula $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+\delta}$ (*n* = 1, 2 and 3) where n imply the number of CuO_2 planes, which results to three bismuth superconducting cuprates $Bi_2Sr_2CuO_{6+x}$ (one CuO_2 plane with T_C=7-22 K), $Bi_2Sr_2CaCu_2O_{8+x}$ (two CuO_2 planes with T_C=85 K) and $Bi_2Sr_2Ca_2Cu_3O_{10+x}$ (three CuO_2 planes with T_C=110 K) abbreviated as Bi2201, Bi2212 and Bi2223 respectively [4]. The maximum T_C increases with increasing number of CuO_2 planes [12, 13, 14]. This gave rise to the expectation that T_C may increase further when the structural cell has more CuO_2 layers [15]. Superconductivity occurs predominantly in

the CuO$_2$ planes.Interlayer and intra-layer interactions in layered HTS Cuprates play an important role in the enhancement of T$_C$ [12, 16, 17],whereas T$_C$ has been found to be proportional to the number of Cu–O layer in Bi–Sr–Ca–Cu–O and Hg–Ba–Ca–Cu–O compounds [13, 20]. Table 1 below shows the number of cuprates plane and the T$_C$ of Bismuth based HTS cuprates.

Table 1. *Bismuth based cuprates phases, their T$_C$ and Number of CuO$_2$ planes.*

CuprateCompound	Short hand notation	MaximumT$_C$ (K)	No of Cuprates planes
Bi$_2$Sr$_2$CuO$_6$	Bi2201	20	1
Bi$_2$Sr$_2$CaCu$_2$O$_8$	Bi2212	95	2
Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10}$	Bi2223	110	3

The Bi-based HTSC are superior to the YBCO in respect of higher T$_C$. This class of superconductors (unlike YBCO) are resistant to water or humid atmosphere and have the advantage of compositional / oxygen stability, e.g. some of its superconducting phases do not gain or lose oxygen, when the material is annealed at 850°C [12]. Another advantage of the BSCCO materials relates to the fact that BiO layers being Van der Waal bonded, this material can be easily rolled. This property has been utilized successfully for tape-casting and its texturing. Furthermore, Bi2223 has been used in making superconducting tape magnet for maglev train [19] and wires for large-scale and high-current applications [20]. This magnet is very successful and a train using this magnet has been shown to achieve a speed of up to 500 km/h [19]. However, it is generally agreed that Bi2212 samples have not reached the degree of purity and structural perfection obtained in YBCO [12]; hence a theoretical study is advised.

2. Theoretical Formulation

The order parameter of an interaction between Cooper pair and electron is given by a ket (1).

$$|\Psi\rangle = \prod_{k,q=1}^{n}\left(u_k + v_k a_k^\dagger a_{-k}^\dagger\right) a_q^\dagger |0\rangle \tag{1}$$

From (1), Cooper pair in momentum state *k,* comprises of two electrons creation operators in state *k*, i.e. spin up $a_k^\dagger$, and spin down $a_{-k}^\dagger$. The independent electron in an excited state *q* is created by $a_q^\dagger$ in a vacuum $|0\rangle$. Note that u_k is the probability of a vacuum state $|0\rangle$ in momentum state *k* being unoccupied by the Cooper pair $a_k^\dagger a_{-k}^\dagger$ whereas, v_k is the probability of a vacuum state $|0\rangle$ in momentum state *k* being occupied by the Cooper pair $a_k^\dagger a_{-k}^\dagger$. The complex conjugate for the order parameter is shown by a bra in (2) below

$$\langle\Psi| = \prod_{k,q=1}^{n}\langle 0|a_q\left(u_k^* + v_k^* a_k a_{-k}\right) \tag{2}$$

The Hamiltonian for the interaction between Cooper pair and an electron based on Froehlich equation is given as

$$\hat{H} = \sum_q \epsilon_q a_q^\dagger a_q + \sum_k \epsilon_k a_k^\dagger a_{-k}^\dagger a_{-k} a_k$$

$$+ \sum_{k,q} V_{k,q}\, a_q^\dagger a_q a_k^\dagger a_{-k}^\dagger - \sum_{k,q} V_{k,q}\, a_q^\dagger a_q a_{-k} a_k$$

$$- \sum_{q,k} U_k\, a_q^\dagger a_k^\dagger a_{-k}^\dagger a_{-k} a_k a_q \tag{3}$$

From (3), ϵ_q and ϵ_k are the kinetic energies for an electron and Cooper pair respectively. $V_{k,q}$ is the positive interaction potential between the electron and the Cooper pairs whereas U_k is the negative Coulomb's potential between the electron and the Cooper pair. The average energy needed during the interaction is written as

$$E_k = \langle\Psi|\hat{H}|\Psi\rangle \tag{4}$$

Inserting (1) and its conjugate (2) as well as (3) into (4) and obeying the anti-commutation rule, the ground state energy E_k is determined.

The following are the conditions for determining specific heat (C_V), Sommerfeld coefficient (γ), entropy (S) and critical temperature (T$_C$) of the system

$$C_V = \frac{dE_n}{dT} \tag{5}$$

$$\gamma = \frac{C_V}{T} \tag{6}$$

$$S = \int C_V \frac{dT}{T} \tag{7}$$

$$\left(\frac{\partial C_V}{\partial T}\right)_{T=T_C} = 0 \tag{8}$$

3. Results and Discussion

3.1. Energy of the System

From figure 1 (a), the energy of a mole of Bi2201, Bi2212 and Bi2223 is 0.747× 10^{-22} J, 3.548× 10^{-22} J, and 4.109×10^{-22} J respectively at the T$_C$.The energy per unit mass is found to be 0.05977 JKg^{-1}, 0.2466 JKg^{-1} and 0.2466 JKg^{-1} respectively at T$_C$ as shown in figure 1(b).The shape of the graph relating energy to temperature in figure 1 is half – stretched sigmoid curves. This shape of curve was also observed by other researchers [13, 14, 21, 22, 23, 24, 25]. For the Bismuth based cuprates, a decrease in temperature results to a decrease in energy (figure 1).The effect of number of particles on the thermal properties of a heavy nuclei system showed that a decrease in temperature leads to a reduced particle interaction with a decrease in energy [26]. This concurs with observations in figures 1, that a decrease in temperature results into a decrease in energy which effectively implies a reduction in particle interaction as a result of reduced temperature. Comparatively the energy at T=T$_C$ for an electron – Cooper pair interaction for Tl2201, Tl2212 and Tl2223 is 3.548×10^{-22}J, 3.922×10^{-22}J, and 4.669×10^{-22}J respectively [13]; whereas the energy of interaction for an electron – Cooper pair at T=T$_C$ is found to be 3.661×10^{-22}J, 4.781×10^{-22}J, and 5.043×10^{-22}J for Hg1201, Hg1212 and Hg1223 respectively [14]. The ARPES measurements on BSCCO indicate a *d*-wave energy gap with

$\Delta_0 \sim 30$ meV [27] and $\Delta_0 \sim 27$ meV [28]. From the comparative results it is noted that the experimental technique applied during experimental measurement determines the likely energy of interaction and it is close to our prediction for Bismuth based cuprates.
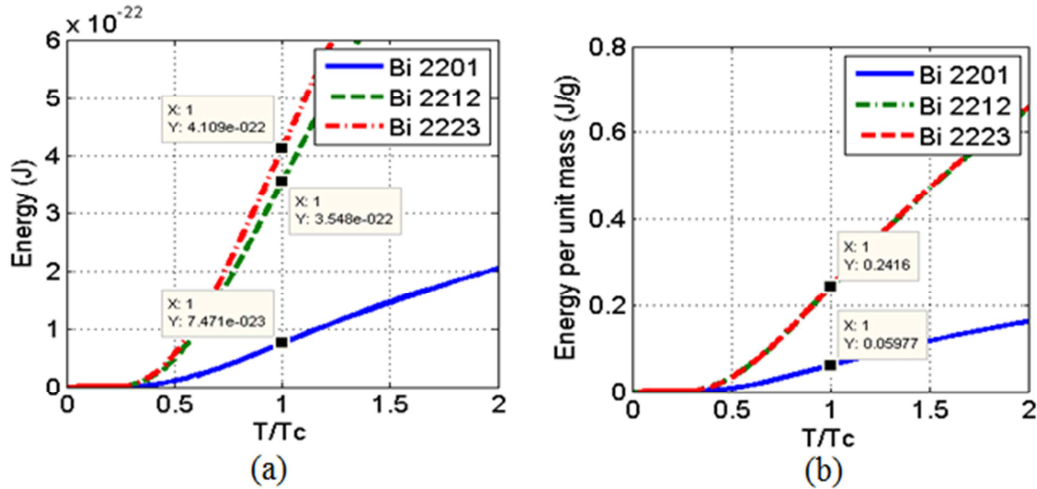

Figure 1. Energy of Bismuth based Cuprates as a function of Temperature (a) for a mole and (b) per unit mass.

3.2. Specific Heat of the System

The graph for specific heat as a function of T/T_C shown in figures 2, are skewed Gaussian shaped curves. This has been observed by other scientists for varied materials under varied conditions [29-31]. The specific heat in a mole of Bismuth based cuprates is found to be 7.471×10^{-24} JK^{-1} at the T_C of Bi2201, Bi2212 and Bi2223 as shown in figure 2 (a). The specific heat per unit mass in Bismuth based cuprates is found to be 5.977mJg^{-1}K^{-1}, 5.064mJg^{-1}K^{-1} and 4.393mJg^{-1}K^{-1} for Bi2201, Bi2212 and Bi2223 as shown in figure 2 (b).Peak specific heat occurs at critical temperature [32].

Comparatively Kibe [22] while studying the pairing symmetry of the singlet and triplet pairing observed specific heat capacity of 4.8×10^{-23} JK^{-1} at T_C. It has been noted that at $T=T_C$, the specific heat for Tl2201, Tl2212 and Tl2223 is 5.337 mJg^{-1}K^{-1}, 4.597 mJg^{-1}K^{-1}, and 4.038 mJg^{-1}K^{-1} respectively [13] whereas Hg1201, Hg1212 and Hg1223 has specific heat per unit mass of 7.463 mJg^{-1}K^{-1}, 5.839 mJg^{-1}K^{-1}, and 4.965 mJg^{-1}K^{-1} respectively [14]. We notice that at the T_C for Bismuth based cuprates just as in the case for Thallium and mercury based HTS, as the number of CuO$_2$ planes increases, the specific heat decreases proportionally [13, 14].
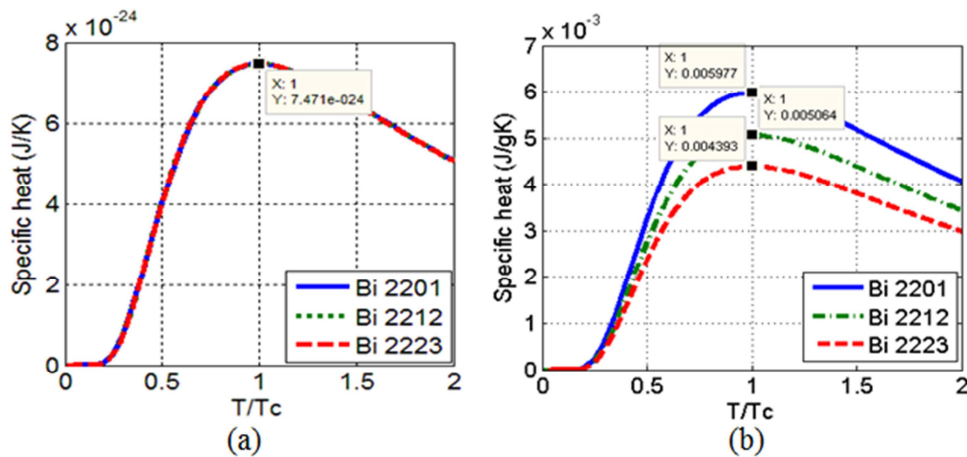

Figure 2. Specific heat for Bismuth based cuprates as a function of Temperature for (a) a mole of Bismuth based cuprates (b) a unit mass of bismuth based cuprates.

3.3. Sommerfeld Coefficient of the System

The Sommerfeld coefficient sometimes called electronic specific heat is a ratio of specific heat to the temperature. In the case of a mole of Bismuth based cuprates it is found to be 4.633×10^{-25} J K^{-2}, 0.9763×10^{-25} J K^{-2} and 0.8432×10^{-25} JK^{-2} at the T_C of Bi2201, Bi2212 and Bi2223 respectively as shown in figure 3 (a). The Sommerfeld coefficient per unit mass in Bismuth based cuprates is found to be 7.413mJg^{-1}K^{-2}, 6.287mJg^{-1}K^{-2} and 5.454mJg^{-1}K^{-2} for Bi2201, Bi2212 and Bi2223 respectively as shown in figure 3 (b).
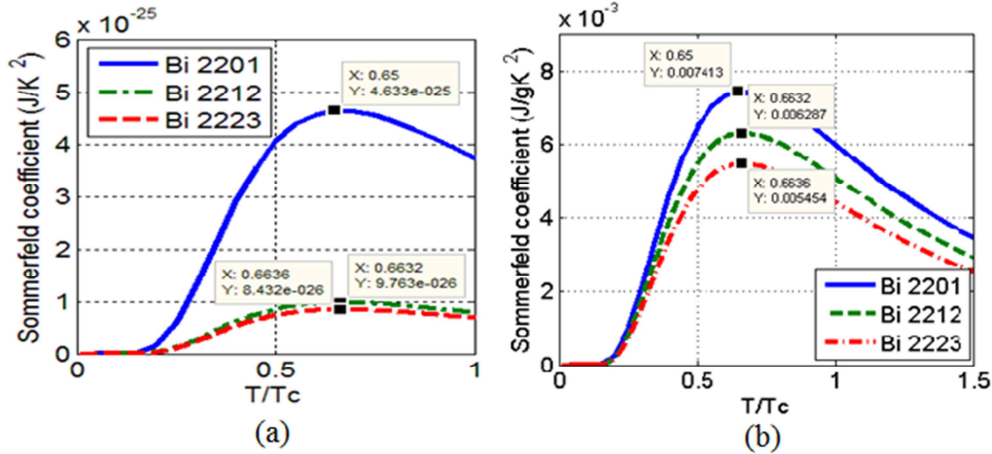
Figure 3. *Sommerfeld coefficient as a function of temperature for Bismuth based cuprates in (a) a mole of BSCCO (b) a unit mass of BSCCO.*

Comparatively the Sommerfeld coefficient for Tl2201, Tl2212 and Tl2223 is $6.975\times10^{-5}Jg^{-1}K^{-2}$; $5.436\times10^{-5}Jg^{-1}K^{-2}$; and $4.01\times10^{-5}Jg^{-1}K^{-2}$ respectively [13]; whereas for Hg1201, Hg1212 and Hg1223 the Sommerfeld coefficient is $9.455\times10^{-5}Jg^{-1}K^{-2}$; $5.664\times10^{-5}Jg^{-1}K^{-2}$ and $4.567\times10^{-5}Jg^{-1}K^{-2}$ respectively[14].The discrepancy between Sommerfeld coefficients arises from different extent of imperfections in samples of HTS cuprates used, as well as from inaccurate normalization that arises from imprecise oxygen composition determination [33, 34]. The structure of bismuth clip rates is very similar to the structure of thallium cuprates such as TI220I, T12212 and TI2223, with bismuth replaced by thallium, and strontium replaced by barium. In spite of similar structural features of bismuth and thallium compounds, there are differences in superconducting and normal-state properties [12]. From figure 3, the peak Sommerfeld coefficient occurs at a truncated temperature $T/T_C=0.6$ for all Bismuth based cuprates. This has also been observed in mercury based cuprates [13], and thallium based cuprates [14].In conclusion, the number of planes of CuO_2 is inversely proportional to theSommerfeld coefficient [13, 14].

3.4. Entropy of the System

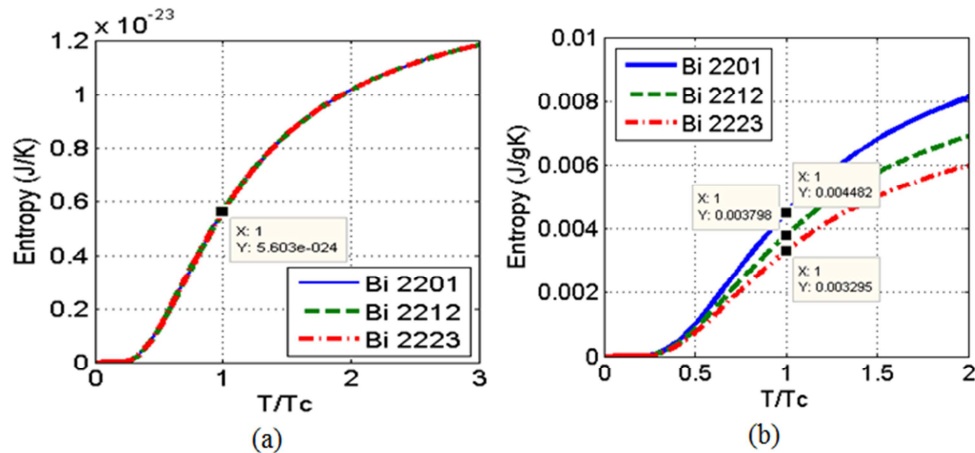Entropy is the disorder experienced in the material media.

In case of a mole of Bismuth based cuprates is found to be $5.603\times10^{-24}JK^{-1}$ at the T_C of Bi2201, Bi2212 and Bi2223 as shown in figure 4 (a). Nearly similar entropy has been found per mole for: YBCO with value 3.036×10^{-24} Junit cell$^{-1}K^{-1}$ [35];whereas Rapando [23] based on theoretical study using the dipole mediated t-J model (t-J-d) found entropy to be $5.04693\times10^{-22}JK^{-1}$. The specific heat per unit mass in Bismuth based cuprates is found to be $4.482\,mJg^{-1}K^{-1}$, $3.798\,mJg^{-1}K^{-1}$ and $3,295\,mJg^{-1}K^{-1}$ for Bi2201, Bi2212 and Bi2223 as shown in figure 4 (b).

When the temperature is lowered from a higher value to a lower value, the entropy also decreases and the HTS Cuprates material becomes more ordered. Other scientists have also made similar observation on the trend of entropy below T_C[13,14, 23, 24]. Comparatively, the entropy for Tl2201, Tl2212 and Tl2223 was found to be 4.003 $mJg^{-1}K^{-1}$, 3.448 $mJg^{-1}K^{-1}$ and 3.028 $mJg^{-1}K^{-1}$ respectively [13], while Hg1201, Hg1212 and Hg1223 had entropy per unit mass of 5.597 $mJg^{-1}K^{-1}$, 4.38 $mJg^{-1}K^{-1}$ and 3.794 $mJg^{-1}K^{-1}$ respectively [14]. From the results, entropy decreases with an increasing number of CuO_2 planes in bismuth based cuprates as observed in thallium based cuprates [13], and mercury based cuprates [14].

Figure 4. *Entropy as a function of temperature for Bismuth based cuprates for (a) a mole BSSCO (b) a unit mass of BSSCO.*

4. Conclusion

In conclusion it'snoted that at T=T$_C$ the energy of interaction in a three electron model in Bismuth based cupratesincreases with an increase in the number of CuO$_2$ planes. It is noted that a decrease in the specific heat per unit mass results in a proportional increase in the number of CuO$_2$ planes. Sommerfeld coefficient decreases with an increase in number of CuO$_2$ planes, Specific heat and entropy per mole are constants not depending on CuO$_2$ planes. When considered per unit mass entropy decreases with an increase in the number of CuO$_2$ planes.

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