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Free Energy, Specific Heat, and Critical Field Calculations for High Temperature Superconductors

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Abstract:
Within the frame work of Ginzburg-Landau theory and the modified BCS theory, the Helmholtz free energy, specific heat, and critical fields were derived. The obtained expressions where then used to compute numerically the free energy, specific heat, and critical fields as a function of temperature using relevant parameters for certain compounds. The results show relatively similar behavior for the two theories. However, the results using the BCS modified theory showed good agreements with some reported experimental results.

Keywords: High Temperature Superconductors, Specific heat, Free Energy, Critical fields, Ginzburg-Landau Theory, BCS Theory.

1. Introduction

Since the discovery of high temperature superconductors (HTSC's) in the ceramic copper oxides (cuprates) by Muller and Bednorz [1], theoretical and experimental attempts were made to explain the mechanism of superconductivity in these compounds, but none of them was fully accepted [1-3]. The difficulty of this problem is due to their complicated properties. With their complicated crystalline structures (layered structures), these HTSC's not only show a relatively high T_c but also show properties that differ from those of the classical (low-temperature) superconductors [4,5]. Theoretical calculations of free energy and specific heat with the available experimental data could provide a better understanding of the fundamental processes involved in the mechanism and behavior of these compounds.

The aim of this article is to compare the as obtained results from Ginzburg-Landau phenomenological theory and the corresponding results as obtained from the microscopic BCS theory.The calculations include Helmholtz free energy, specific heats and critical fields. Then the Helmholtz free energy difference, *Δf* and the specific heat difference, *ΔC$_v$*, will be computed.The obtained results from the two theories will be compared with some available experimental results of some compounds.

Theoretical Background: From basic thermodynamics of superconductors, the free energy density difference between normal and superconducting states in zero field is given by:

$$f_n(0) - f_s(0) = \frac{H_c{}^2(T)}{8\pi} \quad (1),$$

where the subscripts (s) and (n) denote superconducting and normal states. It shows that the critical magnetic field, H_c, is related thermodynamically to the free energy [7,8].

The emperial law of $H_c(T)$ is given by [8]:

$$H_c(T) = H_c(0)[1 - t^2](2),$$

where $t = \frac{T}{T_c}$, is the reduced temperature. The entropy, S, and the specific heat, C_v, are given by:

$$S = -\left(\frac{\partial F}{\partial T}\right)_H (3)$$

$$C_v = T\frac{dS}{dT} = -T\frac{d^2 f}{dT^2}(4).$$

In the absence of any field, the Helmholtz free energy can be written as [9-11]:

$$f_s(T,0) = f_n(T,0) + \alpha(T)|\Psi|^2 + \frac{\beta(T)}{2}|\Psi|^4 + \ldots.. \quad (5),$$

where $|\Psi|$ is an order parameter and α and β are the characteristic expansion coefficients [7]. For $T < T_c$ the coefficient α must be negative and βmust be positive thus, there are two minima at $= \pm\sqrt{\frac{-\alpha}{\beta}}$. Now, by minimizing the free energy, the change in the free energy between the superconducting and normal state is given by:

$$f_s - f_n = -\frac{\alpha^2}{2\beta}(6).$$

The coefficients usually expanded as: $\alpha(T) = \alpha_0 T_c(t-1)$ where α_o = constant > 0 and β can be taken as constant then equation (2.6) becomes [12]:

$$f_n - f_s = \frac{\alpha_0{}^2 T_c{}^2}{2\beta}(t-1)^2 \quad (7).$$

Using equations (2.3) and (2.4), the change in entropy, $S_s - S_n$, and the change in specific heat, $C_s - C_n$, can be written as:

$$S_s - S_n = \frac{\alpha_0{}^2}{\beta} T_c(t-1) \quad (8)$$

$$C_s - C_n = \frac{\alpha_0{}^2}{\beta} T_c \,\mathrm{t} \quad (9).$$

Also, from Eqs. (5), (6) and (7) the thermodynamic critical field, H_c, can be written as:

$$H_c(t) = \sqrt{\frac{8\pi}{2\beta}}\left(-\alpha_0 T_c(t-1)\right)(10) .$$

From Ref. [15], the free energy density difference between the superconducting and normal states, is given by:

$$\frac{f_s - f_n}{N(0)} = -\frac{1}{2}\Delta^2(T) - \Delta^2(T) ln\left[\frac{\Delta(0)}{\Delta(T)}\right] + \frac{1}{3}\pi^2 T^2 - 4Te^{-\frac{\Delta(T)}{T}}\sqrt{\frac{\pi T\Delta(T)}{2}} \times \left[1 + \right.$$

$$38T\Delta(T) - 15128T\Delta(T)2(11).$$

and Δ(0) is given by:

$$\Delta(0) = \frac{\omega_D}{\sinh\left[\sum_{n=0}^{\infty}\frac{4}{(2n+1)\pi}\tan^{-1}\left(\frac{\omega_D}{T_c(2n+1)\pi}\right)\right]}(12),$$

where Δ(0) and Δ(T) are superconducting order parameters (energy gap) at *0K* and T, respectively; *N(0)* is the density of states at Fermi level, since $\hbar\omega_D \ll \epsilon_f$ then $N(0) \approx N(\epsilon_f)$, where ω_D is Debye frequency and ϵ_f is Fermi energy.

In G-L theory there are two characteristic length, the penetration depth (λ) which represents the distance that a magnetic field penetrates a superconductor, and the coherence length (ξ) which represents the size of Cooper pair (according to the BCS theory). The ratio of the two lengths, $\frac{\lambda}{\xi}$, is called the Ginzburg-Landau parameter, K. The parameters α_0 and β are given by[5,16].

$$\alpha_0 = \frac{\hbar^2}{2m_s * T_c * \xi^2(0)} = \frac{0.0305 * 10^{-19}}{T_c * \xi^2(0)} \quad (13)$$

$$\beta = 0.216 * 10^{-51} * K^2 \quad (14)$$

The reported values (Ref. [11, 12, 17] of the parameters T_c, λ and ξ were measured in ab-plane when λ and ξ are parallel to the planes and c- direction when λ and ξ are perpendicular to the planes, therefore, we made the calculations in ab- plane and c-direction independently. We did not consider the change in electron pair mass between ab-plane and c- direction. Also, we did not consider the effect of the thermal fluctuations around the critical temperature. From Eqs (13) and (14) and using the reported data of T_c, λ and ξ we have calculated α_0 and β for several cuprate superconductors then substituted the results directly in Eqs (7), (.9) and (10) to calculate free energy difference, specific heat difference and critical field.

In the BCS modified theory, we used the equation for the free energy difference between superconducting and normal state per density of states, $\frac{f_s - f_n}{N(0)}$, namely,Eqn.12 to derive the corresponding expressions for Δc and Hc; and they are given by:

$$\frac{C_s - C_n}{N(0)} = \frac{-t}{T_c}\frac{d^2}{dt^2}\left[\frac{f_s - f_n}{N(0)}\right]$$

$$= \frac{-t}{T_c}\frac{d^2}{dt^2}\left[-\frac{1}{2}\Delta^2(t) - \Delta^2(t) ln\left[\frac{\Delta(0)}{\Delta(t)}\right] + \frac{1}{3}\pi^2(T_c t)^2 - 4T_c t e^{-\frac{\Delta(t)}{T_c t}}\sqrt{\frac{\pi T_c t \Delta(t)}{2}} \times \left[1 + \frac{3}{8}\left(\frac{T_c t}{\Delta(t)}\right) - \frac{15}{128}\left(\frac{T_c t}{\Delta(t)}\right)^2\right]\right] (15),$$

and,

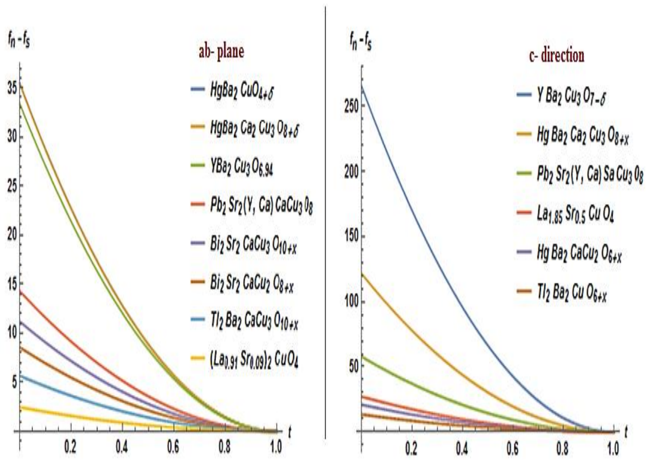
$$\frac{H_c}{\sqrt{N(0)}} = \sqrt{8\pi\left(\begin{array}{c} -\frac{1}{2}\Delta^2(t) - \Delta^2(t) ln\left[\frac{\Delta(0)}{\Delta(t)}\right] + \\ \frac{1}{3}\pi^2(T_c t)^2 - 4(T_c t)e^{-\frac{\Delta(t)}{T_c t}}\sqrt{\frac{\pi T_c t \Delta(t)}{2}} \times \\ \left[1 + \frac{3}{8}\left(\frac{T_c t}{\Delta(t)}\right) - \frac{15}{128}\left(\frac{T_c t}{\Delta(t)}\right)^2\right] \end{array}\right)}$$

(16).

Results and Discussions:

Table-1 shows reported values of λ, ξ and T_c [11, 12] and the calculated α_0 and β for one list of cuprate superconductors (ab- plane). While Table-2shows reported values of λ, ξ andT_c [11, 12, 17], and the calculated α_0 and β for another list (c- direction).

Table-1: Reported values ofλ, ξ and T_c [Ref. 11, 12]and calculated α_0 and β for a list of cuprate superconductors.



Material	λ_{ab} [nm	ξ_{ab} [n	T_c[K]	$\alpha_0[10^{-22}$	$\beta[10^{-47} J.m^3]$
$(La_{0.91}Sr_{0.09})_2C$	283	3.3	30	0.093	0.159
$Pb_2Sr_2(Y,Ca)C$	258	1.5	76	0.178	0.639
$YBa_2Cu_3O_{6.94}$	150	1.7	91.2	0.116	0.168
$HgBa_2CuO_{4+\delta}$	117	2.1	93	0.074	0.067
$Bi_2Sr_2CaCu_2O_8$	200-300	2	94	0.081	0.337
$Bi_2Sr_2Ca_2Cu_3O$	150	2.9	107	0.034	0.058

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$Tl_2Ba_2CaCu_3O$	200	3	125	0.027	0.096
$HgBa_2Ca_2Cu_3($	130-200	1.5	135	0.100	0.261

Table-2: Reported values of λ, ξ and T_c [Ref. 11, 12, 17]and calculated α_0 and β for a list of cuprate superconductors..

Material	$\lambda_c(nm$	$\xi_c(nm$	$T_c(K$	$\alpha_0[10^{-22}$	$\beta[10^{-47}$ J.$m^3]$
$La_{1.85}Sr_{0.5}CuO_4$	400	0.7	40	1.6	7.1
$Pb_2Sr_2(Y,Ca)Cc$	643	0.3	76	4.5	99.2
$Tl_2Ba_2CuO_{6+x}$	2000	0.2	82	9.3	2160
$YBa_2Cu_3O_{7-\delta}$	450	0.2	90	8.5	109.4
$HgBa_2CaCu_2O_6$	800	0.4	127	1.5	86.4
$HgBa_2Ca_2Cu_3O$	700	0.19	135	6.3	293.2

The calculated changes of Helmholtz free energy difference between the superconducting and normal state versus reduced temperature in ab- plane and c-direction are shown in Fig.1.

Figure 1: Free energy difference $(f_n - f_s)$ in units of $[10^4$ (J/m³)] versus reduced temperature (t) in ab- plane and c- direction.

Figure 1 shows that the free energy difference $(f_n - f_s)$ decreaseswithincreasing temperature. It also shows that the value of free energy difference $(f_n - f_s)$ at each reduced temperature, t, for each compound depends on the parameters λ and ξ ($\Delta f \propto \frac{1}{(\xi\lambda)^2}$).

The calculated changes of specific heat difference between the superconducting and normal state with temperature, in ab- plane and c- direction are shown in Fig.2.

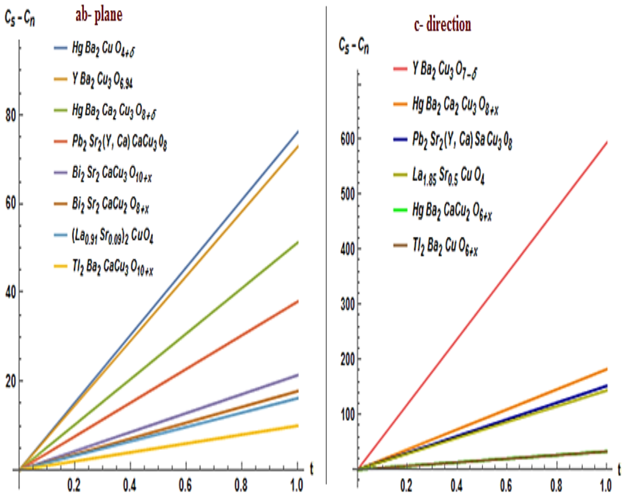

Figure 2: Specific heat $(C_s - C_n)$ in units of $[10^2$(J/ (K. m³)] versus reduced temperature (t) in ab- plane and c- direction.

This figure shows that the specific heat difference $(C_s - C_n)$ is linearly dependent on reduced temperature (t) in accordance with Eq. (9). The slope of these lines is equal to $\frac{{\alpha_0}^2}{\beta}T_c$, which depends on λ, ξ and T_c (the slope $\propto \frac{1}{(\lambda\xi)^2 T_c}$). The values of $(C_s - C_n)$ at $t = 1 or T = T_c$ must give the values of energy gaps $(\Delta C_v(T_c))$ in units of (J/ (K. m³).We have found that the values of free energy difference depends on $(\Delta C_v(T_c))$as follow:

$$f_n - f_s \approx \frac{\Delta C_v(T_c) * T_c}{2} * (t-1)^2$$
(18),

and the relation between all superconducting parameters:

$$\xi^2\lambda^2\Delta C_v(T_c)T_c \approx \pi^2{\varphi_0}^2 = constant.$$
(19)

The calculated change of the thermodynamic critical field with temperature in ab- plane and c- direction is shown in Fig.3.

Table-3: calculated values of H_{c1}, H_{c2} and H_c at 0K in ab- plane and c- direction.									
Material	$K(^{\lambda}/_{\xi}$	$K(^{\lambda}/_{\xi}$	$(H_c(0)$ $[10^{-2}T$	$(H_{c1}(0)$ $[10^{-2}T]$	$(H_{c2}(0)$ $[T]$	$(H_c(0)$ $[10^{-2}$	$(H_{c1}(0$ $[10^{-2}T$	$(H_{c2}(0$ $[T]$
$(La_{0.91}Sr_{0.09})_2$	85.76	----------	24.9	0.91	30.2	----------	----------	----------
$La_{1.85}Sr_{0.5}Cu$	----------	571.4	----------	----------	----------	82.75	0.65	668.7
$Pb_2Sr_2(Y,Ca)$	172	2143.3	59.9	1.27	145.7	120.6	0.31	3655.5
$Tl_2Ba_2CuO_{6+}$	----------	10000	----------	----------	----------	58.16	0.04	8225.1
$YBa_2Cu_3O_{7-\delta}$	----------	2250	----------	----------	----------	258.4	0.63	8222.2
$YBa_2Cu_3O_{6.94}$	88.24	----------	91.7	3.29	114.4	----------	----------	----------
$HgBa_2CuO_{4+}$	55.7	----------	94.5	4.82	74.4	----------	----------	----------
$Bi_2Sr_2CaCu_2$	125	----------	46.4	1.27	82	----------	----------	----------
$Bi_2Sr_2Ca_2Cu_3$	51.7	----------	52.9	2.85	38.68	----------	----------	----------
$Tl_2Ba_2CaCu_3$	66.67	----------	37.8	1.68	35.64	----------	----------	----------
$HgBa_2CaCu_2$	----------	2000	----------	----------	----------	72.7	0.2	2056.3
$HgBa_2Ca_2Cu$	110	3684.2	94.4	2.85	146.85	174.9	0.28	9112.7

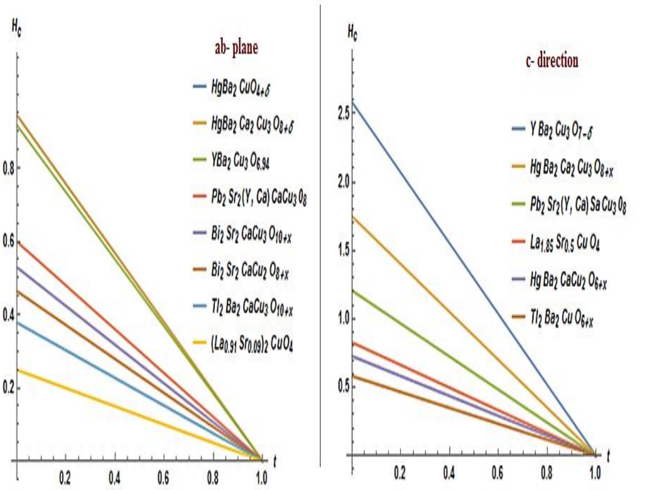

Figure 3: Critical field $H_c(t)$ in units of $[10^{-2}T]$versus reduced temperature (t) in ab- plane and c- direction.

Fig. 3 shows that the thermodynamic critical field $H_c$is linearly dependent on reduced temperature (t) in accordance with Eq. (10). The slope of these lines is equal to $-\alpha_0 T_c\sqrt{\frac{8\pi}{2\beta}}$ and the intercept for each line (which is basically the value of $H_c(0)$) is equal to$\alpha_0 T_c\sqrt{\frac{8\pi}{2\beta}}$ and these values depend on λ, ξ (the slope $\propto -\frac{1}{\lambda\xi}$). The calculated values of $H_c(0)$, $H_{c1}(0)$ and $H_{c2}(0)^*$ for cuprate compoundslisted in Table-1 and Table-2 aresummarized in Table-3.

We have calculated the energy gap values $\Delta(0)$ using Eq. (12) for the set of cuprate superconductors used in this study and utilizing the T_c and ω_D values from Ref 11. The calculated values of $\Delta(0)$ are listed in Table-4.

Table-4: Calculated results of $\Delta(0)$ in units of [meV] from equation (12) versus experimental values of $\Delta_{exp.}(0)$ in units of [meV]. Ref. [19]

Material	$\Delta(0)$ [meV]	$\Delta_{exp.}(0)$ [meV] Ref[19]	Percent error
$(La_{0.925}Ba_{0.0752})_2CuO_4$	4.27	-----	-----
$(La_{0.925}Sr_{0.075})_2CuO_4$	5.95	~ 6.5	9.24
$YBa_2Cu_3O_7$	15.97	~ 16	0.002
$Bi_2Sr_2CaCu_2O_8$	17.81	~ 17.5	0.017
$Bi_2Sr_2Ca_2Cu_3O_{10}$	20.92	~20.5	0.02
$Tl_2Ba_2Ca_2Cu_3O_{10}$	23.91	-----	-----

The calculations of $\Delta(0)$were in good agreement with experimental values.The energy gapto T_c ratio shows a value several times larger than BCS predicted value and approximately equal: $\frac{2\Delta(0)}{k_B T_c} \approx (3.5-5)$which is similar to results mentioned in Ref. [20] for cuprate superconductors.

The calculated change of Helmholtz free energy difference between the superconducting and normal state per density of states with temperature for the cuprate superconductors listed in Table-3 is shown in Fig.4.

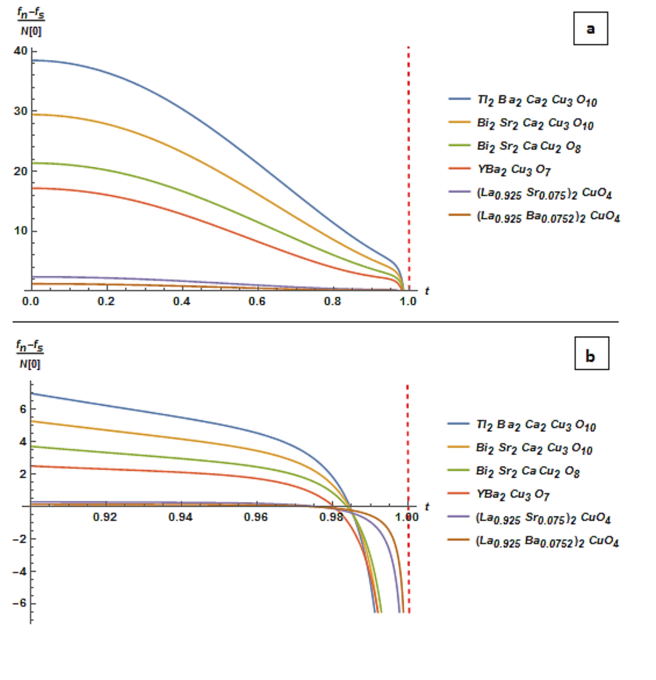

Figure 4: $(f_n - f_s)/N(0)$ in units of $[10^3 K^2]$ vs reduced temperature (t).
Plot range: a. $(0 \rightarrow 1)t$ and b. $(0.9 \rightarrow 1)t$.

Fig. 4 shows that free energy difference per density of states $(f_n - f_s)/N(0)$ decreases with increasing temperature and at temperature close to T_c superconductivity is destroyed. It also shows that the magnitudes of $(f_n - f_s)/N(0)$at certain reduced temperatures depend on T_c and$\Delta(0)$. This could be duetoextremely large thermal fluctuation around T_c.
The calculated change of specific heat difference between the superconducting and normal state per density of states with temperature for the cuprate superconductors listed in Table-3 is shown in Fig.5.

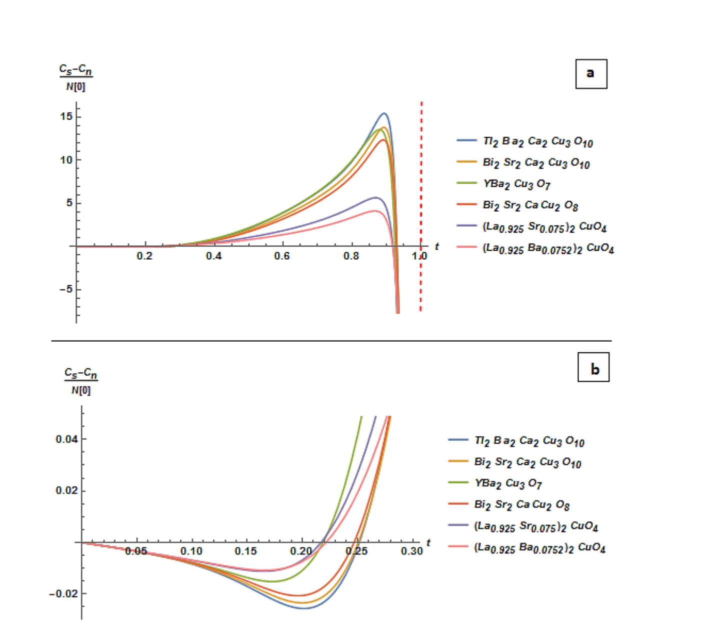

FIG.5: $(C_s - C_n)/N(0)$ in units of$[10^2 K]$vs reduced temperature (t)
Plot range: a. $(0 \rightarrow 1)t$ and b. $(0 \rightarrow 0.3)t$.

Fig.5 shows a hump in specific heat change per density of states $(C_s - C_n)/N(0)$as temperature approachesT_c. At temperatures, well below T_c (when t is within the range $(0 - 0.25)$) the change in specific heat becomes negative i.e. $C_s < C_n$which agrees some experimental evidences. It also shows that the values of $(C_s - C_n)/N(0)$ at certain reduced temperature, t, depends on $\Delta(0)$ and T_c. Similar behavior of $C_s - C_n$ was observed for$YBa_2Cu_3O_{6.92}$,[3] and $Bi_{2.12}Sr_{1.9}Ca_{1.06}Cu_{1.96}O_{8+x}$, [3, 21].

The calculated change of critical field per density of states with temperature for the cuprate superconductors listed in Table-3 is shown in Fig.6.

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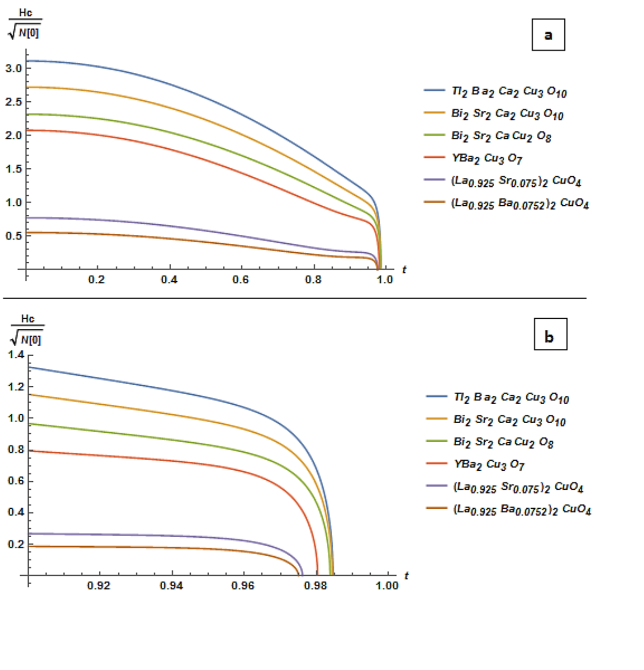

Figure 6: $H_c/N(0)$ in units of $[10^{-2} T * m^{\frac{3}{2}} * \frac{K^{\frac{1}{2}}}{k_B{}^{\frac{1}{2}}}]$ vs reduced temperature (t). Plot range: a. $(0 \to 1)t$ and b. $(0.9 \to 1)t$.

Fig.6 shows that the thermodynamic critical field per density of states $H_c/N(0)$ decreases when increasing temperature and at temperature close to $T_c$it vanishes. It also shows that the values of $H_c/N(0)$at certain reducedtemperature, depends on T_c and$\Delta(0)$.

CONCLUSIONS

In conclusion, we have studied the thermodynamics of cuprate superconductors using Ginzburg-Landau theory and modified BCS theory. Without taking into account the chemical composition of the system or its crystal structure, we found that the free energy difference, the specific heat difference, and critical fields all depend on the parameters T_c, λ, ξ and $\Delta C_v(T_c)$, ; with noticed direct proportionality with T_c and $\Delta C_v(T_c)$and inverse proportionalitytoλ and ξ.By comparing the results in ab- plane and c- direction it is concluded that all the thermodynamic calculations are strongly dependent on the values of the coherence length (ξ) which means that Cooper pairs sizes play important role on the thermodynamic stability of these materials.It has been found that free energy difference, the specific heat difference, and the critical fieldsall dependdirectly onT_c and ω_D. There was agood agreement between the experimental observations and the theoretical calculations. For HTSC's (strong coupling), the lattice plays a role or probably the phonon mediated mechanism is responsible for the pairing of electrons formed in condensed state for HTSC's. We suggest studying the isotope effect of these materials which could help in proving whether the BCS theory is also valid for HTSC's or not.

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