PRAMANA
— journal of
physics

© Indian Academy of Sciences

Vol. 79, No. 6
December 2012
pp. 1495–1501

Effect of oxygen deficiency on the magnetic field-dependent entropy in $YBa_2Cu_3O_{7-\delta}$

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MS received 20 May 2011; revised 27 May 2012; accepted 20 June 2012

Abstract. Roulin *et al* (1988), in one of their experimental papers, have presented a study of field-dependent entropy of high-purity $YBa_2Cu_3O_{7-\delta}$ (YBCO) as a function of oxygen deficiency. In order to explain their experimental results, we have used phenomenological GL-theory of anisotropic HTSCs in the London limit in line with of our earlier paper (Pattanaik *et al*, *Physica* **B405**, 3234 (2010)). Moreover, to account for the applicability of the theory at high field, we have incorporated the effect of vortex overlapping in the London theory done by Nanda (1995). Here, we have presented the variation of change in entropy (ΔS) with magnetic field for different oxygen deficiencies $\delta = 0$, 0.04, and 0.06. On comparison, we found that our results are in good agreement with the experimental data of Roulin *et al* (1988). The variation of penetration depth (λ) and anisotropic ratio of effective masses (γ) with concentration is also presented.

Keywords. High-T_c superconductors; phenomenological theory; anisotropic properties.

PACS Nos **74.72.−h; 74.25.Ha; 74.70.Wz**

1. Introduction

The origin of the unusual magnetic field dependence of specific heat in the high-T_c superconductors (HTSCs) has been the subject of investigations from the time of its discovery [1–3]. Experiments on HTSCs show that the specific heat anomaly near the superconducting transition temperature T_c is reduced in amplitude with negligible downward shift in temperature by the application of magnetic field B_a ($\sim$1 T) [4–8]. This behaviour is distinctly different from the conventional type-II superconductors. It is shown recently that the unusual magnetic field dependence of the specific heat anomaly in HTSCs can arise due to a very general reason on the basis of three-dimensional description of the phenomenological Ginzburg–Landau (GL) theory of anisotropic type-II superconductors [9]. The anisotropy in the 'field dependence' was shown to be directly related to the penetration depths $\gamma(=\lambda_c/\lambda_{ab})$ and the effective masses $\gamma(=m_c/m_{ab})^{1/2}$. Here, m_c and m_{ab} are the components of the dimensionless effective mass tensor parallel and

DOI: 10.1007/s12043-012-0353-y; ***e*Publication: 13 September 2012**

perpendicular to the c-axis and $\lambda_{c,}$ λ_{ab} are the penetration depths along c-axis and ab-plane directions respectively.

It is observed that the oxygen vacancy in YBCO is very sensitive to the critical temperature (T_c) and the anisotropic ratio (γ). Some of the experimental results on YBCO show that the oxygen concentrations do influence some of the physical properties such as specific heat, entropy, resistivity, and physical parameters such as coherence length (ξ), penetration depth (λ) etc. of the HTSCs [10–12]. The work of Fuchs *et al* [10] on YBCO revealed that the effect of oxygen concentration on resistivity, superconducting transition temperature (T_c) and upper critical field (B_{c2}) greatly influence the value of δ. They have also shown that when δ values increase from 0 to 0.4, the value of T_c decreases and it disappears when $\delta = 0.5$. They have reported that for δ values greater than zero, there is a broadening of transition curve. Further, in the presence of magnetic field an additional broadening is observed for the transition curve which they have accounted due to the anisotropy of the upper critical field B_{c2}. Ossandon *et al* [11] have reported that oxygen concentration do influence the superconducting magnetization (M), critical current density (J_c), irreversibility field (V_{irr}), upper critical field (B_{c2}), coherence length (ξ), penetration depth (λ) and related properties as a function of temperature as well as applied magnetic field along crystallographic c-axis. In the study of the effect of oxygen deficiency on specific heat in YBCO system by Roulin *et al* [12], it is observed that T_c and γ values increase as the doping changes from the over-doped $\delta = 0$ to under-doped $\delta = 0.06$. Thus, it is shown that for different concentrations of oxygen, i.e. for $YBa_2Cu_3O_7$, $YBa_2Cu_3O_{6.96}$, $YBa_2Cu_3O_{6.94}$ the value of T_c increases from 88 K at $\delta = 0$ to 90 K at $\delta = 0.04$ and 93 K at $\delta = 0.06$ respectively. Similarly, they have estimated that the anisotropic ratio decreases from 8 to 5. In this paper, we have concentrated on the work of Roulin *et al* [12] to explain theoretically the influence of δ on entropy and anisotropic ratio as a function of field and temperature.

In this paper, we have tried to analyse from the expression of change in entropy and specific heat in magnetic field the general orientation of B_a with respect to the crystallographic c-axis using the phenomenological GL theory as done in one of our earlier papers [13] and have discussed in §2. Moreover, we have analytically derived the simple relation of the anisotropy as a function of δ and incorporated the vortex correction of Nanda [14] into it which is given in §3. To avoid the complexity we have ignored the anisotropy in the ab-plane.

2. Phenomenological GL theory

The anisotropic properties of oxide and layered HTSCs residing in the mixed state in lower applied magnetic field below the transition temperature is explained theoretically using anisotropic London equation as well as GL theory. GL theory is effective in explaining the mixed state near the upper critical field but it fails close to lower critical field [15], due to which, within London limit and temperature close to transition, GL approach with phenomenological mass tensor can be approximated for studying mixed state with lower applied magnetic field. Under this circumstance, the assumed order parameter $|\psi|$ is spatially constant. Taking random orientation of the applied field for polycrystalline layered structures, different field- and temperature-dependant parameters can be well explained using the concept of anisotropic mass tensor. In view of this, Kogan and co-workers [16,17] used anisotropic London theory and found partial accomplishments with some demarcations [18]. Investigating different effects, Campbell and Kogan [19,20] included anisotropy in the effective mass tensor on Helmholtz free energy for the superconductor. The specific heat enhancement due to applied magnetic field is a derivative of entropy change [21]. Hence, taking the relationship between H and B in terms of reduced effective mass tensor, the expression for change in entropy and change in specific heat has been established particularly for Dy-based cuprate superconductor [13].

$$\Delta S = -\frac{2\alpha B\gamma^{-1/3}\varepsilon(\theta)}{\lambda_m^2(0)T_c} \ln\left[\frac{e\gamma B_{c2}^{\|c}}{\varepsilon(\theta)}\right] \tag{1}$$

$$\langle \Delta C\rangle = \frac{B_a}{T_c}\frac{t}{(1-t)}\frac{\alpha\Theta(\gamma)}{\lambda_m^2(0)}. \tag{2}$$

Keeping all the terms as earlier for getting the expression of entropy change of the above form, we have used GL parameter dependences [9] of mean penetration depth and upper critical field as

$$\lambda_m(T) = \frac{\lambda_m(0)}{2^{1/2}}(1-t)^{-1/2} \quad \text{and} \quad B_{c2}(T) = B_{c20}(1-t)\,. \tag{3}$$

Using eq. (1), the observed specific heat anomaly near the transition temperature with applied field was explained quantitatively for the Dy-123 system [13]. Encouraged by its success with this formalism we have later explained the anomalies in specific heat and entropy for other two systems Y-123 and Nd-123 which gave good results [22,23]. Here, in this paper, we have tried to explain the effect of oxygen deficiency (δ) on these systems as some experimental observations show evidence that δ do affect various system parameters of HTSCs. In doing so, we derived the concentration dependence of penetration depth assuming that the change in specific heat is a linear dependence of concentration as observed in different experiments [11,12]. The detailed analytical derivation of $\lambda(\delta)$ is given in §3. For further improvement over our calculation the vortex overlapping effect has been incorporated in line with Nanda [14]. With this, the penetration depth now becomes the function of both δ as well as vortex correction factor through λ_{eff} as given in eq. (12) of §3. Since γ is related to the penetration depth ($= \lambda_c/\lambda_{ab}$), it can also be related in terms of δ. To start with, in this paper, we have analysed the δ dependence of entropy change as well as γ for YBCO system only. Moreover, the different notations involved in the above equations are the same as that of our earlier paper [13].

3. Analytical solution for δ (oxygen deficiency) dependence of γ

Since the value of T_c shifts as the value of concentration δ changes, for simplicity we redefine the new T_c values in the following way.

Let,

$$T_{ci} = T_{c0} + \Delta_i, \tag{4}$$

where T_{c0}, T_{c1} and T_{c2} are the critical temperatures at the concentration (δ) values for $i = 0$, 0.04 and 0.06 respectively and Δ_i is the change in T_c value with respect to δ_0. We can now express eq. (2) as

$$(\Delta C)_i = \frac{B_a}{T_{ci}} \frac{t_i}{(1-t_i)} \frac{\alpha\theta(\gamma)}{\lambda_m^2(0)}. \tag{5}$$

Now substituting the value of T_{ci} as defined in eq. (4) we can express eq. (5) as

$$\langle \Delta C \rangle_i = \frac{B_a}{T_{c0}+\Delta_i} \left(\frac{T}{T_{c0}+\Delta i} \Big/ 1 - \frac{T}{T_{c0}+\Delta i} \right) \frac{\alpha\Theta(\gamma)}{\lambda_m^2(0)}. \tag{6}$$

$(\Delta_i/T_{c0}) = \eta_i$, where η_i is a very small quantity and is equal to 0 for $i = 0$. Performing the binomial expansion in the above equation one can express eq. (6) as

$$\left\{ \frac{B_a}{T_{c0}} \left(\frac{t_i}{1-t_i} \right) (1-\eta_i)^2 + \frac{B_a}{T_{c0}} \eta_i \, (1-\eta_i)^2 \left(\frac{t_i}{1-t_i} \right)^2 \right\} \frac{\alpha\Theta(\gamma)}{\lambda_m^2(0)}. \tag{7}$$

To compare eq. (7) with eq. (2) we keep the linear term neglecting the second which is quadratic in t $(= T/T_{c0})$, i.e.

$$\langle \Delta C \rangle_i = \frac{B_a}{T_{c0}} \left(\frac{t_i}{1-t_i} \right) \frac{\alpha\,\theta\,(\gamma)}{\lambda_m^2\,(\eta_i)}, \tag{8}$$

where

$$\lambda_m(\eta_i) = \frac{\lambda_m(0)}{(1-\eta_i)}. \tag{9}$$

Since Δ (change in T_c) $\propto \delta$ (concentration) so also $\eta_i \propto \delta_i$ since $\eta_i = \Delta_i/T_{c0}$. Hence

$$\lambda_m = (\delta_i) = \frac{\lambda_m(0)}{(1-\delta_i)}. \tag{10}$$

Further, to make the theory more appropriate one can incorporate the effect of vortex overlapping as at higher applied field there is a strong interaction between the vortices and the interspacing between the vortices decreases affecting the value of λ_m to a new effective value given by eq. (2) of ref. [14]

$$\lambda_{\text{eff}}^2 = \frac{\lambda_m^2}{(1-b)}, \tag{11}$$

where $b = B/B_{c2}$. Now replacing the value of $\lambda_m(0)$ to $\lambda_{\text{eff}}(0)$ given in eq. (11) we can re-express eq. (10) as

$$\lambda_m(\delta_i) = \frac{\lambda_{\text{eff}}(0)}{(1-\delta_i)} = \frac{\lambda_m(0)}{(1-\delta_i)\,(1-b)^{1/2}}. \tag{12}$$

Since anisotropy is related to the penetration depth we can assume γ also to vary in similar fashion as

$$\gamma_i = \frac{\gamma(0)}{(1-\delta_i)}. \tag{13}$$

Equations (12) and (13) express the oxygen deficiency dependences of penetration depth (λ) and anisotropic ratio (γ) taking vertex overlapping.

4. Results and discussions

Here, we have presented the change in entropy (ΔS) with applied magnetic field and variation of anisotropic ratio (γ) for different oxygen deficiencies for high-purity YBCO sample and compared with the experimental work of Roulin *et al* [12]. In the experimental work, Roulin *et al* [12] have presented the change in specific heat (ΔC) for high-purity YBCO with applied magnetic field parallel to c-axis for three concentrations 7.0, 6.96, 6.94, i.e. for $\delta = 0, 0.04, 0.06$. It is observed from the ΔC vs. T plot, that T_c increases from 88 K to 92 K and to 93 K as the concentration decreases from 7 to 6.96 and to 6.94 respectively. Here, we have compared the change in entropy with different fields and concentrations with our theoretical calculations from eq. (1). Since the change in entropy is equal to the area of the curve of $(\Delta C/T)$ vs. T, the change in entropy (ΔS) is evaluated by plotting the curve $(\Delta C/T)$ vs. T for each of the curve given by Roulin *et al* [12]. Then by using the standard values for YBCO, i.e. $T_c = 91.2$ K, $T = 85$ K, $e = 2.78$, $B_{c2}^{\parallel c} = 8.3$ and the molar volume of YBCO as 6.38 g/cm^3 [9] in eq. (1), the change in entropy (ΔS) is calculated and compared with the experimental values from Roulin *et al* [12] for different concentrations and fields. This is presented in table 1 as well as in figures 1a–c. In this connection it is to be pointed out that Roulin *et al* [12] have given three plots (figures 1, 2, 3 of their paper) for the variation of change in specific heat with temperature at different applied fields each with a specific concentration. However, the variations of magnetic fields taken in these figures are not identical in these plots. For a comparison, the values of magnetic field must be consistent and same in three plots. On analysing these plots we find that the magnetic fields 1, 2, 3, 6, 9, 12, 14, 16 T are common to all the three plots. However, it is observed that for the field 6 T and beyond, the comparison is not good because of which we avoided these fields taking only three fields, i.e. 1, 2 and 3 T. This may be due to the inaccuracy in value of the calculated area for obtaining entropy from the experimental curves or vortex overlapping may not be working in such high fields.

Table 1. Data of change in entropy for different oxygen concentrations along with respective values of applied magnetic field.

Conc.	Field	Change in entropy	
$x = 7 - \delta$	(T)	Calculated	Expt.
7.00	1	37.069	32.605
	2	57.682	62.279
	3	72.246	65.538
6.96	1	36.857	25.182
	2	57.352	69.199
	3	71.833	97.647
6.94	1	36.751	48.898
	2	57.187	63.935
	3	71.626	103.795

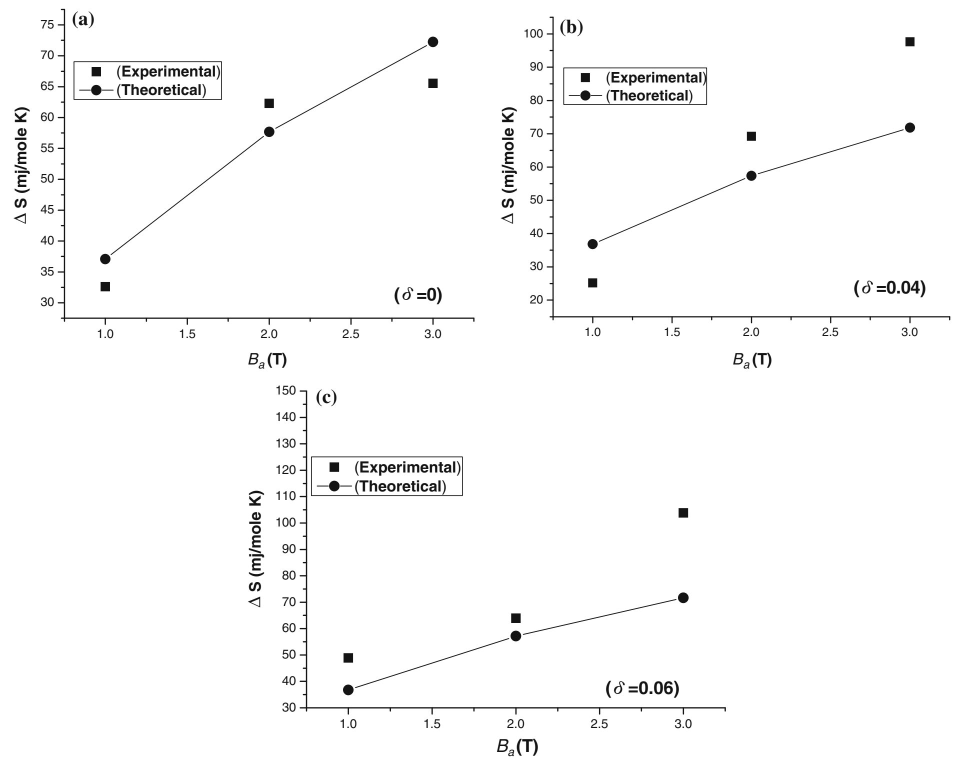

Figure 1. (**a**) Variation of change in entropy (ΔS) with different applied fields for $x = 7$, (**b**) variation of change in entropy (ΔS) with different applied fields (for $x = 6.96$) and (**c**) variation of change in entropy (ΔS) with different applied fields for $x = 6.94$.

Accounting the effect of δ on anisotropic ratio we analytically showed the variation of γ with the same. Moreover, in HTSCs it is observed that in the intermediate range, the flux density B increases with increase in applied field and the interspacing between the vortices decreases, hence the overlapping between the vortices becomes stronger by increasing the magnetic interaction range. The effective penetration depth originates from the overlap of the vortices. At low average flux density B, effective penetration depth reduces to the weak field penetration depth. With increase in applied field effective penetration depth increases and diverges at the upper critical field B_{c2} [14]. So to make the theory applicable both at high and low fields, we have incorporated the vortex overlapping and replaced the value of penetration depth with the effective penetration depth for calculating both penetration depth as well as anisotropy of effective masses.

5. Summary

Here we have compared the calculated values of change in entropy with the applied fields in three concentrations with the experimental values and found that the values are in good agreement in small fields but not so in higher fields. Further, we have incorporated the vortex overlapping into the usual London theory for its application in higher applied fields. Beside this, penetration depth as well as anisotropic ratio as a function of oxygen concentration has been established.

Acknowledgement

One of the authors (PN) acknowledges the DRS-I of UGC under SAP running in the School of Physics, Sambalpur University, Odisha, India.

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