Oxygen reordering near room temperature in YBa$_2$Cu$_3$O$_{6+x}$: A thermodynamic model

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We propose a thermodynamic model to explain an unusual phase transformation occurring near room temperature in YBa$_2$Cu$_3$O$_{6+x}$ that greatly affects properties of the superconductor. Based on our model, the material's thermodynamic response functions, specific heat, thermal-expansion coefficient, and elastic compliances are deduced at the critical temperature of the phase transformation. We discuss the change of critical temperature with stress, and analyze the anomaly of specific heat in critical temperature of the phase transformation.

I. INTRODUCTION

The superconducting and normal-state properties of YBa$_2$Cu$_3$O$_{6+x}$ (YBCO) depend strongly on both oxygen stoichiometry and the degree of oxygen order in the CuO chain layers. For example, the "two plateau" phenomena, a "plateau" of superconducting transition temperature $T_c \approx 90$ K with an oxygen content $x > 0.85$, and second one of $T_c \approx 60$ K for $x \approx 0.45$–0.65,[1,2] relate to two types of oxygen-ordered orthorhombic structure, ortho I, and ortho II,[3] respectively. Oxygen ordering can engender charge transfer between the CuO$_x$ and CuO$_2$ planes, entailing a rise of the superconducting transition temperature T_c.[4–9] Various theoretical models[10–23] and experimental techniques[23–29] have been used to study normal oxygen ordering in YBCO, from the disordering to the ordering critical temperature T_c' about 1000 K. In substoichiometric YBCO oxides ($x < 1$), other oxygen ordering transformations, such as ortho I to ortho II or ortho III, and so on also were demonstrated experimentally[23,30,31] and analyzed theoretically.[11,13–16,18,22,32,33] However, another phase transformation, occurring about 220–280 K, which relates to the discontinuous change of material's lattice constants,[34] specific heat,[35,36] elastic stiffnesses,[37–40] electrical resistivity,[41] and dielectric constant,[42] has only been revealed experimentally. Although most experimenters deemed that this phase transformation is related to the reordering of oxygen atoms,[34–41] it has no theoretical explanation until now. In this paper, we suggest a thermodynamic framework and lattice distortion mechanism to explain this oxygen-reordering process and then discuss some thermodynamic response functions on either side of the critical temperature of the phase transformation.

II. THERMODYNAMIC MODEL

Oxygen ordering in YBCO consists of the redistribution of oxygen atoms over two equivalent sublattices of the interstitial sites located in the basal Cu-O (001) plane [Fig. 1(a)]. In the disordered tetragonal T phase, oxygen atoms are randomly distributed over the α and β sites; therefore the oxygen concentrations in these sites are $c_\alpha = c_\beta = c/2$ (c is the concentration of oxygen atoms in the Cu-O plane, c_α and c_β are, respectively, the concentration of oxygen atoms in the α and β sites). Oxygen ordering entails changes in oxygen

concentration at both sites. Oxygen atoms predominantly occupy one of the types of sites, and, concurrently, the structure is transformed from the tetragonal to the orthorhombic phase, as shown in Figs. 1(b) and 1(c), which are two energetically equivalent variants with different directional orientations. This oxygen-ordering process has been explored by several methods, mean-field approximation,[16–18] quasichemical,[19–21] and cluster variation.[10–15] However, sometimes these two comparable sites, α and β, will become nonequivalent, for instance, when an external uniaxial stress is applied in the x or y axis of YBCO, or its internal electronic structure is changed. Then, the *a priori* probabilities of oxygen atoms occupying α and β sites will differ. Therefore the oxygen-ordering process in the Cu-O plane with nonequivalent α and β sites becomes different from the usual process with equivalent sublattice sites.[43] A phase transformation will occur if the unbalanced process of occupancy of α and β sites is associated with a change in temperature or application of uniaxial stress. Because this phase transformation originates from lattice distortion, it will be called the strain-induced oxygen reordering (SIOR) phase transformation. The Gibbs free energy G of this SIOR phase transformation, based on mean-field approximation, is written as[43]

$$
\begin{aligned}
G(\eta) = {} & \frac{1}{2}(zv_1\eta^2 + v_2\eta) + \frac{1}{2}RT\{(2c+\eta)\ln(2c+\eta) \\
& + (2c-\eta)\ln(2c-\eta) + [2(1-c)+\eta] \\
& \times \ln[2(1-c)+\eta]+[2(1-c)-\eta]\ln[2(1-c)-\eta]\} \\
& + \frac{1}{2}\sum_{ijkl}C_{ijkl}\varepsilon_{ij}\varepsilon_{kl} - \sum_{ij}\sigma_{ij}\varepsilon_{ij},
\end{aligned}
\tag{1}
$$

where R is the gas constant and z is the coordination number of the α or β sites. η is the long-range order parameter, defined as $\eta = c_\alpha - c_\beta$. Considering only the interaction between the nearest-neighbor and next-nearest-neighbor oxygen and vacancies,

$$
v_1 = \left[v_{ov}^{(1)} - \tfrac{1}{2}\left(v_{oo}^{(1)} + v_{vv}^{(1)}\right)\right] - \tfrac{1}{2}\left[v_{ov}^{(2)} - \tfrac{1}{2}\left(v_{oo}^{(2)} + v_{vv}^{(2)}\right)\right], \tag{2}
$$

and

$$
v_2 = (v_{o\alpha} - v_{o\beta}) + (v_{v\beta} - v_{v\alpha}). \tag{3}
$$

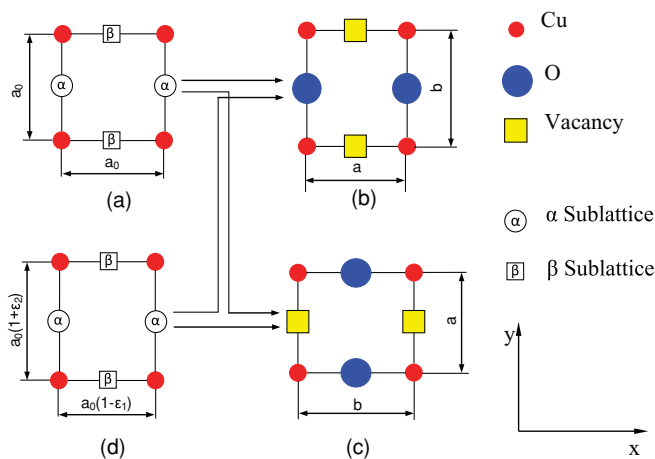$v_{ov}^{(i)}$, $v_{oo}^{(i)}$, and $v_{vv}^{(i)}$ are, correspondingly, the oxygen-vacancy,

FIG. 1. (Color online) A schematic sketch of α sites and β sites from equivalence to nonequivalence. (a) Original square structure; α and β sites are in equivalence. (b), (c) Rectangle structures, a and b sites, respectively, showing regular oxygen occupancy. (d) Original square structure is strained; α sites and β sites have become nonequivalent.

oxygen-oxygen, and vacancy-vacancy pairwise interaction energy, while the superscript "(i)" represents the ith near neighbors. $v_{o\alpha}$ is the energy change resulting from placing an oxygen atom on an α site, i.e., the "formation" energy of an oxygen atom on an α site; $v_{o\beta}$, $v_{v\alpha}$, and $v_{v\beta}$ are similarly designated. We will ignore the influence of variations of temperature and lattice constants on v_1. v_2 is the energy difference of oxygen and vacancies occupying α or β sites. The first term is the oxygen ordering energy discussed above. The second term is the contribution from the configurational entropy of oxygen, based on mean-field theory. The last two terms of Eq. (1) are the distortion energy arising from the ordering process $\frac{1}{2}\sum_{ijkl}C_{ijkl}\varepsilon_{ij}\varepsilon_{kl}$ and the work of an external or internal stress $-\sum_{ij}\sigma_{ij}\varepsilon_{ij}$. A simplified approximation in Cu-O planes of YBCO is

$$\begin{aligned}\varepsilon_{11} &= \varepsilon_0(c_\alpha - c), \\ \varepsilon_{22} &= \varepsilon_0(c_\beta - c),\end{aligned} \qquad (4)$$

where $\varepsilon_0 = \frac{b-a}{b+a}$ ($b > a$) is a strain constant (which can be obtained from lattice parameters) when the oxygen concentration is known. In our case, $\varepsilon_{12} = 0$. Then we have

$$\begin{aligned}\frac{1}{2}\sum_{ijkl}C_{ijkl}\varepsilon_{ij}\varepsilon_{kl} - \sum_{ij}\sigma_{ij}\varepsilon_{ij} &= \frac{1}{4}(C_{11} - C_{12})\varepsilon_0^2\eta^2 \\ &\quad - \frac{1}{2}(\sigma_{11} - \sigma_{22})\varepsilon_0\eta.\end{aligned} \qquad (5)$$

If we define new variables

$$v_1' = v_1 + \frac{C_{11} - C_{12}}{2z}\varepsilon_0^2 \qquad (6)$$

and

$$v_2' = v_2 - (\sigma_{11} - \sigma_{22})\varepsilon_0, \qquad (7)$$

Eq. (1) becomes simplified and can be written

$$\begin{aligned}G(\eta) = {}&\tfrac{1}{2}(zv_1'\eta^2 + v_2'\eta) + \tfrac{1}{2}RT\{(2c + \eta)\ln(2c + \eta) \\ &+ (2c - \eta)\ln(2c - \eta) + [2(1 - c) \\ &+ \eta]\ln[2(1 - c) + \eta] + [2(1 - c) - \eta] \\ &\times \ln[2(1 - c) - \eta]\}.\end{aligned} \qquad (1')$$

When v_1' is negative and v_2' is zero, the temperature will have a critical value T_c', below which there will be three real roots for η at each temperature: one with $\eta = 0$, corresponding to an unstable state, and two other nonzero values of η, one positive and one negative, corresponding to states of stable equilibrium long-range order. The energy of the two stable states is equal. The degeneracy of the energy is broken when $v_2' \neq 0$ at a critical temperature θ_c and one of the sublattices is favored energetically. At this time, a phase transformation occurs. The long-range order parameter will change from η_1 (the order parameter before phase transformation) to η_2 (that after phase transformation). Figure 2 schematically explains the change of free energy during the phase transformation from $v_2' = 0$ to $v_2' \neq 0$. Obviously, v_2 depend on stress, and the critical temperature of the phase transformation is the function of stress. In the absence of strain, the model reduces to the well-known mean-field theory of the tetragonal orthorhombic in YBCO.

The thermodynamic response functions can be deduced from Eq. (1). The contribution from change of oxygen ordering to the specific heat at constant external stress, $c_\sigma = -T[\partial^2 G(\eta)/\partial T^2]$, is

$$c_\sigma = \begin{cases} A_1 T \frac{\partial \eta_1}{\partial T} - B_1 T \left(\frac{\partial \eta_1}{\partial T}\right)^2 & \text{for } T > \theta_c \\ A_2 T \frac{\partial \eta_2}{\partial T} - B_2 T \left(\frac{\partial \eta_2}{\partial T}\right)^2 - \frac{1}{2}T\eta_2 \frac{\partial^2 v_2'}{\partial T^2} & \text{for } T < \theta_c. \end{cases} \qquad (8)$$
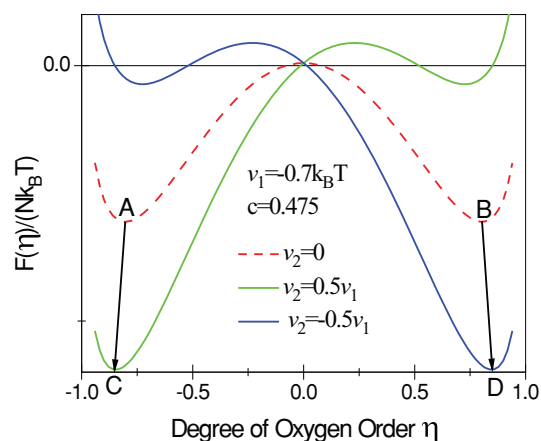

FIG. 2. (Color online) Free energy as function of degree of oxygen order η, according to a mean-field approximation Eq. (1). Dashed line corresponds to $v_2 = 0$; solid lines are for $v_2 \neq 0$. A phase transformation occurs from A or B state to C or D state when v_2 changes from zero to nonzero.

The contribution from the change of oxygen ordering to the thermal-expansion coefficients, $\alpha_{ij} = -\partial^2 G/\partial\sigma_{ij}\partial T$, are

$$\alpha_{ij} = \begin{cases} \frac{1}{2}A_1\frac{\partial\eta_1}{\partial\sigma_{ij}} - B_1\frac{\partial\eta_1}{\partial\sigma_{ij}}\frac{\partial\eta_1}{\partial T} & \text{for } T > \theta_c \\[2mm] -\frac{1}{2}\frac{\partial v_2'}{\partial\sigma_{ij}}\frac{\partial\eta_2}{\partial T} - \frac{1}{2}\eta_2\frac{\partial^2 v_2'}{\partial\sigma_{ij}\partial T} & \text{for } T < \theta_c \end{cases} \tag{9}$$

and the contributions from the change of oxygen ordering to elastic compliances, $s_{ijkl} = -\partial^2 G(\eta)/\partial\sigma_{ij}\partial\sigma_{kl}$, are

$$s_{ijkl} = \begin{cases} -B_1\frac{\partial\eta_1}{\partial\sigma_{ij}}\frac{\partial\eta_1}{\partial\sigma_{kl}} & \text{for } T > \theta_c \\[2mm] -B_2\frac{\partial\eta_2}{\partial\sigma_{ij}}\frac{\partial\eta_2}{\partial\sigma_{kl}} - \frac{1}{2}\left(\frac{\partial v_2'}{\partial\sigma_{ij}}\frac{\partial\eta_2}{\partial\sigma_{kl}} + \frac{\partial\eta_2}{\partial\sigma_{ij}}\frac{\partial v_2'}{\partial\sigma_{kl}} + \eta_2\frac{\partial^2 v_2'}{\partial\sigma_{ij}\partial\sigma_{kl}}\right) & \text{for } T < \theta_c, \end{cases} \tag{10}$$

where η_1 and η_2 in Eqs. (8)–(10) are obtained by minimizing the free energy $G(\eta)$. Thus the condition $\partial G(\eta)/\partial\eta = 0$ gives

$$\ln\frac{(2c-\eta_1)[2(1-c)-\eta_1]}{(2c+\eta_1)[2(1-c)+\eta_1]} = \frac{2zv_1'\eta_1}{RT} \text{ for } T > \theta_c, \tag{11a}$$

$$\ln\frac{(2c-\eta_2)[2(1-c)-\eta_2]}{(2c+\eta_2)[2(1-c)+\eta_2]} = \frac{2zv_1'\eta_2 + v_2'}{RT} \text{ for } T < \theta_c. \tag{11b}$$

From Eq. (11a), we obtain

$$\frac{\partial\eta_1}{\partial T} = \frac{A_1}{2B_1}, \tag{12a}$$

$$\frac{\partial\eta_2}{\partial T} = \frac{A_2}{2B_2}, \tag{12b}$$

$$\frac{\partial\eta_1}{\partial\sigma_{ij}} = 0, \tag{12c}$$

and

$$\frac{\partial\eta_2}{\partial\sigma_{ij}} = -\frac{\frac{\partial v_2'}{\partial\sigma_{ij}}}{2B_2}, \tag{12d}$$

where

$$A_1 = R\ln\frac{(2c-\eta_1)[2(1-c)-\eta_1]}{(2c+\eta_1)[2(1-c)+\eta_1]}, \tag{13a}$$

$$B_1 = 2RT\left[\frac{c}{4c^2-\eta_1^2} + \frac{1-c}{4(1-c)^2-\eta_1^2}\right] + zv_1', \tag{13b}$$

$$A_2 = R\ln\frac{(2c-\eta_2)[2(1-c)-\eta_2]}{(2c+\eta_2)[2(1-c)+\eta_2]} - \frac{\partial v_2'}{\partial T}, \tag{13c}$$

$$B_2 = 2RT\left[\frac{c}{4c^2-\eta_2^2} + \frac{1-c}{4(1-c)^2-\eta_2^2}\right] + zv_1'. \tag{13d}$$

Using Eq. (12), we simplify Eqs. (8)–(10).

$$c_\sigma = \begin{cases} \frac{A_1^2}{4B_1}T & \text{for } T > \theta_c \\[2mm] \frac{A_2^2}{4B_2}T - \frac{1}{2}T\eta_2\frac{\partial^2 v_2'}{\partial T^2} & \text{for } T < \theta_c, \end{cases} \tag{14}$$

$$\alpha_{ij} = \begin{cases} 0 & \text{for } T > \theta_c \\[2mm] -\frac{A_2}{4B_2}\frac{\partial v_2'}{\partial\sigma_{ij}} - \frac{1}{2}\eta_2\frac{\partial^2 v_2'}{\partial\sigma_{ij}\partial T} & \text{for } T < \theta_c, \end{cases} \tag{15}$$

$$s_{ijkl} = \begin{cases} 0 & \text{for } T > \theta_c \\[2mm] \frac{1}{4B_2}\frac{\partial v_2'}{\partial\sigma_{ij}}\cdot\frac{\partial v_2'}{\partial\sigma_{kl}} - \frac{1}{2}\eta_2\frac{\partial^2 v_2'}{\partial\sigma_{ij}\partial\sigma_{kl}} & \text{for } T < \theta_c. \end{cases} \tag{16}$$

From Eqs. (14)–(16), the changes of specific heat, thermal-expansion coefficient, and elastic compliances can be calculated if v_2 is known.

Figure 2 shows the phase transformation from the A or B to C or D state. (The parameters used in Fig. 2 were chosen purely for illustration.) Similar phase transformations, such as magnetic order, sublattice melting, and superconductivity transition due to the coupling between the lattice and electron system, have been studied previously.[44–52] Testardi[44] proposed a thermodynamic theory to describe the behavior of the elastic modulus, thermal-expansion coefficient, and specific heat at this type of phase transformation. Based upon Testardi's model,[44] we write v_2 as

$$v_2(T,\sigma_{ij}) = \phi(\sigma_{ij})\left(1 - \frac{T^2}{\theta_c(\sigma_{ij})^2}\right)^2, \tag{17}$$

where the parameters $\phi(\sigma_{ij})$ and $\theta_c(\sigma_{ij})$ are functions of stress σ_{ij}.

Using Eqs. (14)–(16), and an external stress of zero, the changes across the phase transition of specific heat, thermal-expansion coefficients, and elastic compliances at $T \to \theta_c^-$ and $T \to \theta_c^+$ are

$$\Delta c_\sigma = -\frac{4\phi\eta_2}{\theta_c}, \tag{18}$$

$$\Delta\alpha_{ij} = \frac{4\phi\eta_2}{\theta_c^2}\frac{\partial\theta_c}{\partial\sigma_{ij}}, \tag{19}$$

$$\Delta s_{ijkl} = -\frac{4\phi\eta_2}{\theta_c^2}\frac{\partial\theta_c}{\partial\sigma_{ij}}\frac{\partial\theta_c}{\partial\sigma_{kl}}. \tag{20}$$

Combining Eqs. (18) and (19), the Pippard equation[53,54] is obtained:

$$\Delta\alpha_{ij} = -\frac{\Delta c_\sigma}{\theta_c}\frac{\partial\theta_c}{\partial\sigma_{ij}}. \tag{21}$$

III. DISCUSSION

We noticed that several researchers reported different critical temperatures for the SIOR phase transformation. From Eq. (21), we obtain

$$\theta_c = \theta_{c0} \exp\left(-\frac{\Delta\alpha_{ij}}{\Delta c_\sigma}\sigma_{ij}\right), \qquad (22)$$

where θ_{c0} is the critical temperature at $\sigma_{ij} = 0$. Equation (22) denotes that the critical temperature changes exponentially with an external or internal stress field in an YBCO sample. Several factors will cause internal stress in YBCO. First, Johnson *et al.*'s experiment[55] proved that inhomogeneous oxygen distribution is a general feature of YBCO samples with nonstoichiometry composition. It causes different critical temperatures of SIOR phase transformation in different areas. Because the SIOR phase transformation is associated with a change of lattice constants, the untransformed areas will restrict the occurrence of the phase transformation in other areas, implying that an extra driving force should be present to overcome this restriction when SIOR phase transformation takes place. Second, if the structure of the material also is inhomogeneous, for example, containing twins, grain boundaries, a stress field will be established in various areas of the phase transformation, and possibly will obstruct or enhance the occurrence of the phase transformation.

Despite many reports on the SIOR phase transformation,[34–42] the values of changes in specific heat, the thermal-expansion coefficients, and the elastic compliances during phase transformation are seldom reported. The exceptions are Nagel *et al.*'s[34] measurements of the thermal-expansion coefficients in untwinned single crystals, and the work of Cankurtaran and his co-workers,[37,38] who assessed the changes in elastic stiffness in an isotropic polycrystal sample. Nagel *et al.* estimated an upper limit of the change of the specific heat at about 0.8–2 J/(mol K). Accordingly, the anomaly of specific heat should be detectable experimentally; nevertheless, even high-resolution measurements failed to do so.[56] After carefully checking Nagel *et al.*'s calculation, we consider their estimate excessive. It was derived from the difference in maximum entropy between the totally oxygen-ordered state and the totally disordered state. According to our calculations (using Semenovskaya and Khachaturyan's data[18] about the interaction between oxygen ions pairs in the CuO plane), the degree of oxygen order approaches the totally ordered state at 300 K. Indeed, the change in degree of oxygen order is small (as Fig. 2 shows, the difference in the degree of oxygen order between A and C, and the B and D are small) during the SIOR phase transformation; therefore the contribution of oxygen order to the specific heat is limited. Nevertheless, according to our thermodynamic model, v_2's contribution to the specific heat should be considered (without applied stress). If it is small, it is possible that changes in the specific heat cannot be detected.

Next, we reassess specific heat using Eqs. (18)–(20), and Nagel *et al.*'s[34] and Cankurtaran *et al.*'s experimental data.[37] For the isotropic case, Eqs. (19) and (20) can be rewritten as

$$\Delta\alpha = -\frac{\Delta c_p}{T_c}\frac{\partial T_c}{\partial p}, \qquad (23)$$

$$\frac{\Delta B}{B^2} = \Delta\alpha\frac{\partial T_c}{\partial p}, \qquad (24)$$

where B is the bulk modulus, α is the volume coefficient of expansion, and p is the pressure. Then we obtain

$$\Delta c_p = -\frac{\Delta\alpha^2 T_c B^2}{\Delta B}. \qquad (25)$$

Using $\Delta\alpha = 33 \times 10^{-7} \text{K}^{-1}$ (Ref. 34), $|\Delta B/B| = 0.15$ (Ref. 37), and $B = 47.4$ GPa (Ref. 37), we determine that the change of specific heat in the SIOR phase transformation is about 0.1 J/(mol K). This value is an order of magnitude lower than Nagel *et al.*'s estimate, verifying that detecting specific heat is difficult.

So far, we do not know the microscopic origin of the oxygen-reordering phase transformation, i.e., that change which results in a nonzero value of v_2. Values of v_1 have been discussed in the literature[10–18] and used to explain thermodynamic phase separations (such as ortho I ↔ ortho I + ortho III) using mean-field theory[16–18] and asymmetric-next-nearest-neighbor interaction (ASYNNI) model.[10–15] Some researchers[37] guessed that the SIOR phase transformation is ortho I ↔ ortho I + ortho III transformation. However, the phase separation requires oxygen diffusion and will take a long time at the low temperature of the transformation. Therefore it is difficult to measure the anomaly of thermodynamic response functions due to the phase separation. We think the SIOR phase transformation probably originates from the change in electronic structure. Some experiments, using scanning tunneling microscopy (STM),[57,58] nuclear magnetic resonance (NMR),[59] and nuclear quadrupole resonance (NQR),[60,61] have proved that the charge density wave associated with CuO chain subsystem exists, and that the charge density wave relates to oxygen-vacancy ordering in CuO chains.[62] It is obvious that the interaction between the charge density waves and lattice vibrations will greatly affect superconducting properties.

The result of such a change entails the equivalent change in energy of the two oxygen-occupying sites. This is analogous to applying an external magnetic field during the magnetic-phase transition. We conjecture that the mechanism by which the SIOR transition occurs is either coherent lattice shear, as in martensitic transitions, or perhaps the motion of twin boundaries, and oxygen rearrangement with small activation barriers (see Fig. 2).

IV. CONCLUSION

The change from equivalence to nonequivalence of two oxygen-occupying sites leads to a strain-induced oxygen reordering (SIOR) phase transformation occurring around room temperature in YBCO. The phase transformation yields the change of specific heat, thermal-expansion coefficient, and elastic compliances. The critical temperature of the phase transformation is sensitive to stress. According to the changes in the thermal-expansion coefficient and elastic stiffness measured experimentally, we can conclude that the change of specific heat is small near the critical temperature of the phase transformation.

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