Thermochimica Acta, 174 (1991) 281–297
Elsevier Science Publishers B.V., Amsterdam

HEAT CAPACITIES OF HIGH-T_c OXIDE SUPERCONDUCTORS

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(Received 7 September 1989)

ABSTRACT

A brief review of recent thermodynamic studies of the high-T_c oxide superconductors is presented, focusing attention on heat capacity below room temperature. An historical survey shows that calorimetric measurements have played an important role in research into the properties of superconductors and the mechanism of the superconducting phase transition. Immediately after the pioneering work on La–Ba–Cu–O by Bednorz and Müller (Z. Phys. B, 64 (1986) 189) and the subsequent discovery of superconductivity above 90 K in $YBa_2Cu_3O_{7-\delta}$, much effort has been devoted to the observation of the heat capacity anomaly due to the superconducting phase transition, which should give decisive evidence of bulk superconductivity. The precisely measured curves of the heat capacities can be analyzed, also in order to clarify the mechanism of superconductivity. More recent studies on high quality samples and on newly found compounds have provided further information.

INTRODUCTION

Immediately after the discovery of superconductivity in La–Ba–Cu–O by Bednorz and Müller [1], much effort has been devoted to answering the fundamental question whether the properties are of intrinsic bulk superconductivity or interfacial phenomena. It is well known that the disappearance of electrical resistivity [1], and even the observation of Meissner expulsion of the magnetic flux, can result not from the bulk but from minor superconducting phases which exist as interfacial grain-boundary portions throughout the sample. The question must thus be answered by measuring the heat capacity, which should show an anomaly at the superconducting phase transition for bulk superconductivity. Some attempts [2–6] have failed to detect the heat capacity anomaly because of rather low precision in the measurements and/or poor quality of the samples in an early stage of this field of research, and misconceptions have arisen that a new mechanism might be responsible for high-T_c superconductivity. At the same time, however, heat capacity anomalies due to superconducting phase transitions have been observed for the ceramics of La–M–Cu–O (where M ≡ Ca, Ba or

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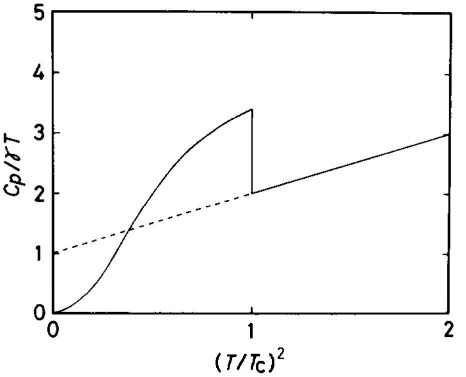

Fig. 1. Schematic variation of the heat capacity of a conventional superconductor at low temperatures.

Sr) in several laboratories [7–14]. For the subsequent compound $YBa_2Cu_3O_{7-\delta}$ with a higher T_c (above 90 K), which was discovered in February 1987 [15–17], bulk superconductivity has also been confirmed by measuring heat capacity anomalies [18,19].

Further important information can be deduced from the heat capacity data, which is recognized on the basis of BCS theory applied to a conventional superconductor, as shown in Fig. 1. In the normal state above T_c, the electronic heat capacity is given as $C_{e,n} = \frac{1}{3}\pi^2 D(\epsilon_F)k^2T = \gamma T$ (D is the electronic density of states at the Fermi level ϵ_F and γ is the electronic heat capacity coefficient), and the lattice heat capacity is approximately represented as $C_l = 3R4\pi^4T^3/5\Theta_D^3 = \alpha T^3$ in the low temperature region ($T \leq \Theta_D/20$; Θ_D is the characteristic Debye temperature). As the total heat capacity is $C = \gamma T + \alpha T^3$, a graph of C/T versus T^2 should be a straight line of gradient α and extrapolation of $T \to 0$ should give an intercept value of γ. In the superconducting phase, an energy gap exists at the Fermi level and the electronic heat capacity has exponential dependence on the temperature. Thus the curve of C/T versus T^2 becomes zero for $T \to 0$. As the temperature increases, however, the energy gap decreases and disappears at the superconducting phase transition, which is of second-order type associated with a jump in the heat capacity value. The heat capacity jump at the superconducting phase transition is related to the electronic heat capacity coefficient as $\Delta C = 1.43\gamma T_c$ in the weak coupling limit of BCS theory.

As such important information is expected to be obtained by thermodynamic investigation, increasing attention has been paid to heat capacity measurements of the high-T_c oxide superconductors. However, there have been few reliable data published so far. A comparison made in December 1987 [20] is shown by way of example in Fig. 2, where some heat capacity data of $YBa_2Cu_3O_{7-\delta}$ are given together. As seen clearly in Fig. 2, the data

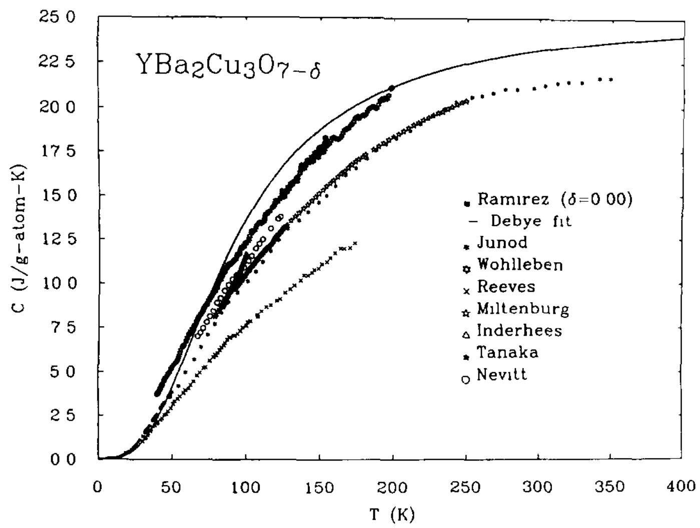

Fig. 2. Comparison of the heat capacities of $YBa_2Cu_3O_{7-\delta}$ measured by different investigators [20].

differ widely. It must be noted that careful review is necessary before using heat capacity data in detailed analysis.

In this article, the questions which are expected to be solved by measuring heat capacities will be described for the high-T_c oxide superconductors, and some representative reports will be presented. More recent studies will be also given concerning high precision measurements on high quality samples and on newly found compounds. A complete survey cannot be possible at this stage, and it is to be regretted that only those references which are known to the author will be cited.

QUESTIONS EXPECTED TO BE SOLVED

The questions which are expected to be solved by measuring the heat capacities of high-T_c superconductors are as follows.

(1) Heat capacity anomaly at T_c: bulk superconductivity has been confirmed by detecting an anomaly in the heat capacity curve. However, questions still remain as to clarification of the mechanism of the superconductivity. How large is the anomaly? Is the shape of the anomaly of typical second-order type as expected from BCS theory?

(2) Heat capacity curve in the lowest temperature region: this is the linear term problem, which gives a finite intercept value in the graph of C_p/T versus T^2 for $T \rightarrow 0$ (see Fig. 1). Is that intrinsic to the superconducting state? Is it possible to explain the origin in terms of resonating-valence-bond theory or a tunneling model of a two-level system?

(3) Effects of magnetic elements: superconductivity is scarcely affected by substitution of rare earth elements for Y in $YBa_2Cu_3O_{7-\delta}$, even those with magnetic spins. In the case of some rare earth elements with magnetic spins, long range magnetic ordering is expected to show a heat capacity anomaly in the superconducting state at low temperatures. Schottky type anomalies are also probable, owing to crystal electric field splitting of the 4f electron energy levels.

(4) Fluctuation phenomena: high resolution heat capacity measurements at the superconducting phase transition enable us to see details of the shape of the anomaly, which would be due to fluctuation phenomena as a deviation from the BCS-type anomaly.

(5) Thermodynamic functions: valuable chemical thermodynamic functions such as heat capacity, enthalpy, entropy and Gibbs energy should be established by precise calorimetry for a wide temperature region (from liquid helium temperatures up to room temperature). The heat capacity value itself is also useful for studying electronic states, the lattice vibration spectrum, and so on.

(6) Effects of oxygen deficiency: a remarkable feature of high-T_c oxide superconductors is nonstoichiometry in the compounds, i.e. oxygen deficiency is counterbalanced mainly by a change in valence of copper atoms (1 or 2). The intrinsic properties of the superconductors are substantially influenced by oxygen deficiency. In the case of $YBa_2Cu_3O_{7-\delta}$, the T_c value decreases as δ increases and an intermediate phase (the so-called orthorhombic II phase) may exist for $\delta \approx 0.4$ with $T_c \approx 60$ K. Further deduction of oxygen atoms leads to the tetragonal phase for $\delta \approx 1$, which is a semiconductor.

(7) Heat capacities under magnetic fields: heat capacity measurements under various magnetic fields provide detailed information about the splitting of the energy levels of magnetic ions. The heat capacities can be analyzed by separating the magnetic and crystal field contributions from the electronic and lattice vibrational terms.

HEAT CAPACITY ANOMALIES AT T_c

At an early stage in the research into high-T_c superconductors, emphasis was put on detection of the heat capacity anomaly due to the superconducting phase transition at T_c, which must be the definitive evidence for bulk superconductivity [7–14,18,19]. Extensive studies have been reported along this line [21–30]. Theoretical attempts [31–34] have also been made to estimate the upper limit on the heat capacity jump and other thermodynamic properties concerning the mechanism of superconductivity, which might be considerably distant from those predicted by BCS theory which is

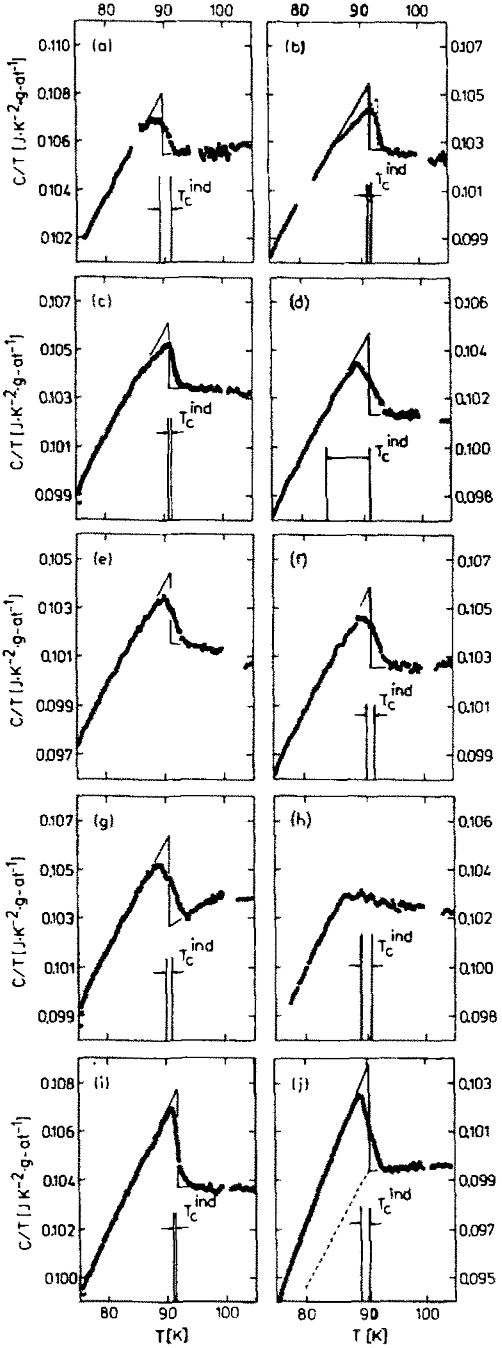

Fig. 3. Heat capacity anomalies due to the superconducting phase transition of $YBa_2Cu_3O_{7-\delta}$ prepared by various techniques [35].

applicable to conventional superconductors. The resonating-valence-bond picture predicts only a cusp in the heat capacity curve without a jump at T_c.

The value of the heat capacity jump at T_c is the most reliable quantitative indication of the quality of the ceramic sample, because it is directly proportional to the amount of the superconducting portion in the sample. The proportionality constant is as yet unknown, however, as parameters such as the Sommerfeld constant and the coupling strength have not been available independently. Optimization of the heat capacity jump at T_c has been studied systematically for a number of polycrystalline samples of $YBa_2Cu_3O_{7-\delta}$ by Junod et al. [35]. Various preparation techniques were tested. Their heat capacity data are shown in Fig. 3. A correlation was established between the magnetic susceptibility of the normal state and the heat capacity jump at T_c. For a better sample, a larger jump is observed, and the largest jump is reported as $\Delta C/T_c = 57$ mJ K^{-2} mol^{-1}. The effect of doping with iron has also been studied in detail for superconductivity in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ [36].

Somewhat strange or rather funny data [37,38] have been reported for $YBa_2Cu_3O_{7-\delta}$ samples which show two anomalies associated with double peaks in the heat capacity around T_c. A hysteretic phase change has been observed between 160 K and 70 K during cooling and between 170 K and 260 K during warming [39]. Glasslike dynamic behavior has also been reported [40].

A striking aspect is that substitution of other rare earth elements for Y in $YBa_2Cu_3O_{7-\delta}$ scarcely influences superconductivity in $MBa_2Cu_3O_{7-\delta}$ (M are rare earth elements) [41,42]. Some reliable data for the heat capacities of such substituted compounds have been obtained by using a high precision adiabatic calorimeter [10,43–46]. The heat capacities of $DyBa_2Cu_3O_{7-\delta}$ [44] are shown in Fig. 4. A comparison of the heat capacity anomalies are given for M ≡ Dy, Er or Tm in Fig. 5 [47]. The critical temperatures and the heat

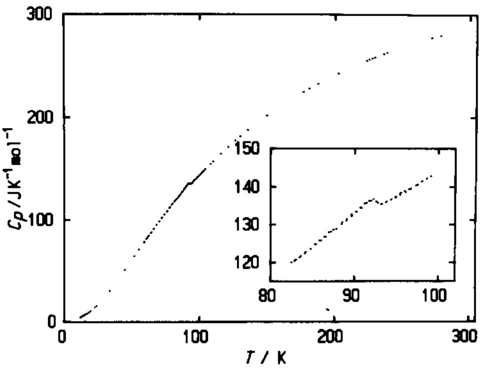

Fig. 4. Heat capacities of $YBa_2Cu_3O_{7-\delta}$ measured using a high precision adiabatic calorimeter [44].

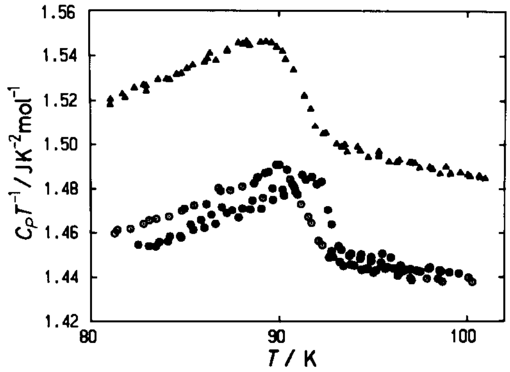

Fig. 5. Heat capacity anomalies due to the superconducting phase transitions of $MBa_2Cu_3O_{7-\delta}$ [47]. M = Dy (●), Er (⊙) or Tm (▲).

capacity jumps of the superconducting phase transitions have been determined from the data, and are given in Table 1. The compound where M ≡ Dy has the highest T_c value, while its heat capacity jump is the smallest. Thus a compound substituted by a heavier rare earth element shows a larger heat capacity jump at a lower T_c value. The shape of the anomaly for M ≡ Dy is, however, very clear and sharp compared with those of the other elements. To clarify this, further systematic investigations are required for well-synthesized samples of a series of compounds substituted by other rare earth elements.

Some studies have been carried out for oxide superconductors with T_c below 40 K [48,49], and also in comparison with the higher T_c components [50]. More recently, new types of compounds, Bi-type and Tl-type, have been discovered, and soon thereafter the heat capacity measurements were made [51–56]. Although bulk superconductivity has been confirmed by detecting heat capacity anomalies [51,52,55,56], detailed analyses are impossible as yet because of the poor quality of the samples, which should not be expected to exhibit their intrinsic properties. Such studies are still in progress for the new compounds [56].

TABLE 1

Heat capacity jump at the superconducting phase transition T_c of $MBa_2Cu_3O_{7-\delta}$ (M ≡ Dy, Er or Tm)

M	T_c (K)	$\Delta C_p/T_c$ (mJ K^{-2} mol^{-1})
Dy	92.5	42
Er	91.2	50
Tm	90.9	56

HEAT CAPACITY CURVES IN THE LOWEST TEMPERATURE REGION

The so-called linear term problem was pointed out at the initial stage of this series of investigations [2,3,6,7], and has been studied extensively in comparison with other properties such as the heat capacity jump at T_c [24,29,30,50]. The linear term γT would originate from the normal state portion which might exist together with the superconducting portion below T_c in the sample (see Fig. 1). Paramagnetic impurities can also cause an extraneous contribution to the heat capacity at the lowest temperatures. In such cases, therefore, the contribution of linear term should be less for a better superconducting sample. Some reports have been published on this problem for La–M–Cu–O (M ≡ Ba or Sr) [48,49,57–59], and the Fermi-liquid-type excitations [48] or the resonating-valence-bond picture [59] were suggested.

For $YBa_2Cu_3O_{7-\delta}$, which is inherently non-magnetic, a number of efforts have been made to obtain the heat capacity curves in detail in the lowest temperature region [24,29,30,60–69]. The heat capacities of several samples obtained by Eckert et al. [69] are shown in Fig. 6, where the unusual sample dependent linear term and the upturn in C_p/T for $T \rightarrow 0$ are clearly seen. They also performed heat capacity measurements on $YBa_3Cu_2O_7$, Y_2BaCuO_5, CuO and $BaCuO_{2+x}$, which might exist as impurities in the superconductors. It has been concluded that the anomalous heat capacity is due at least partly to the presence of $BaCuO_{2+x}$ as an impurity in the samples. However, the fact that the remaining linear term should be of the intrinsic properties of the superconductors cannot be ruled out. The two-level tunneling model systems are also suggested for the origin of the linear term,

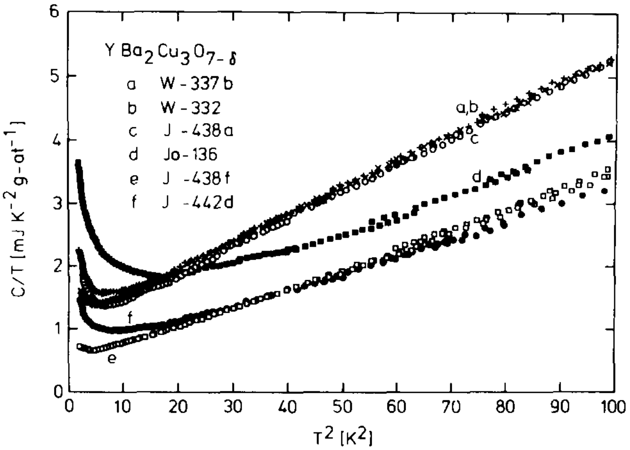

Fig. 6. Heat capacities in the lowest temperature region. The samples of $YBa_2Cu_3O_{7-\delta}$ have been prepared by various techniques [35,69].

as expected in a glassy state [70]. To observe the thermodynamic properties in more detail, some doped samples $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ have also been studied [36,71].

The newly found compounds, Bi-type and Tl-type, have provided a good opportunity to clarify this problem by comparison with the compounds of Y–Ba–Cu–O. In contrast to the previous high-T_c compounds, no appreciable linear term has been reported for the new compounds [52,72–74], and some attempts have been made to analyze the thermodynamic properties on the basis of BCS theory.

EFFECTS OF MAGNETIC ELEMENTS

A remarkable feature of high-T_c oxide superconductors is the fact that the superconductivity is little affected by the existence of magnetic elements substituted for Y in the compounds $MBa_2Cu_3O_{7-\delta}$ (where M ≡ magnetic rare earth elements). Such behavior is unusual in the conventional superconductors where a magnetic element is a "dangerous" impurity. Extensive studies therefore have been carried out to characterize the relevant magnetic interaction in the compounds [50,75–89]. The magnetic ordering has been observed as a sharp anomaly in the heat capacity curve in the lowest temperature region. It has been reported that the ordering temperature varies according to the de Gennes factor, implying that the spin–spin interaction is dominant [81], and the heat capacity anomaly can be represented on the basis of 2-dimensional Ising model [84,85]. A result reported by Simizu et al. [85] is shown in Fig. 7. It has been pointed out by Lee et al. [86], however, that a successful explanation involving the de Gennes factor may be a fortuitous consequence of the effect of reduced degeneracy of the

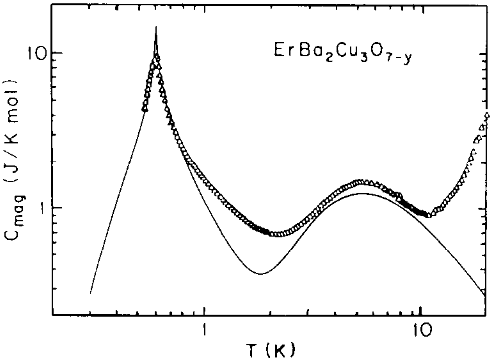

Fig. 7. Magnetic contribution to the heat capacities of $ErBa_2Cu_3O_{7-\delta}$ at low temperatures. Triangles are the data of experiments. The solid line denotes the calculated value of the 2-dimensional Ising model with $|J_{2d}/k| = 0.53$ K and 1-dimensional Ising model with $|J_{1d}/k| = 13$ K [85].

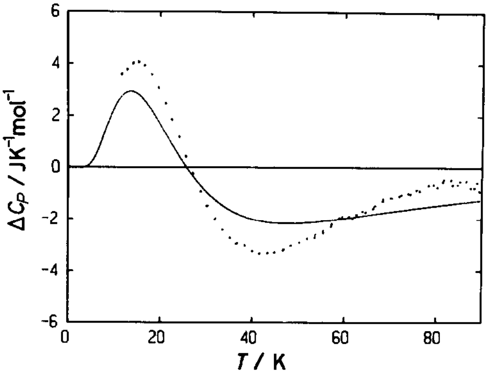

Fig. 8. Heat capacity differences, $C_p(DyBa_2Cu_3O_{7-\delta}) - C_p(ErBa_2Cu_3O_{7-\delta})$, due to Schottky anomalies. The solid line is obtained by a simple two level scheme with energy gaps of 40 K for Dy and 90 K for Er [43].

ground states of the rare earth ions, and magnetic ordering is responsible for the dipole–dipole interaction as suggested by Dunlap et al. [79].

The magnetic rare earth elements should be expected to exhibit another contribution to the heat capacity, i.e. the so-called Schottky anomaly caused by the electric crystal field splitting of the 4f electron levels. Schottky anomalies have been demonstrated for some compounds of $MBa_2Cu_3O_{7-\delta}$ (M ≡ Dy, Ho or Er) by Dunlap et al. [79]. At higher temperatures, the effects have been analyzed on the basis of precise and reliable data by Saito et al. [43]. Their results are shown in Fig. 8, where the heat capacity differences between those compounds where M ≡ Dy and M ≡ Er are given together with a theoretical curve obtained for a simple two-level scheme with

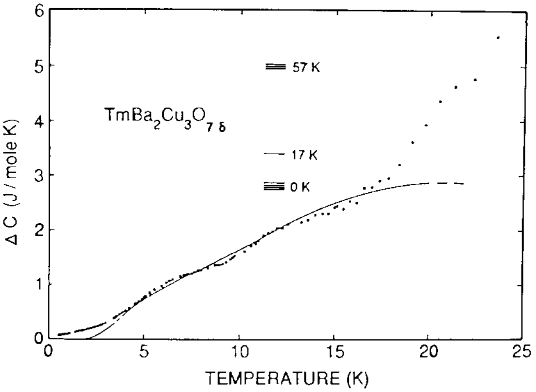

Fig. 9. Excess heat capacities of $TmBa_2Cu_3O_{7-\delta}$ obtained by subtracting the heat capacities of $YBa_2Cu_3O_{7-\delta}$. The solid line represents the calculated Schottky anomalies associated with Tm^{3+} energy levels as shown in the figure [90].

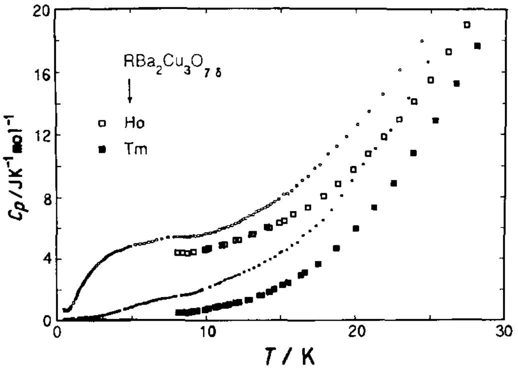

Fig. 10. Comparison of the heat capacity data obtained by Ferreira et al. [90] (small symbols) and those obtained by Atake et al. [45,46,94] (large symbols).

energy gaps of 40 K for Dy and 90 K for Er, assuming the other contributions of lattice vibrations and electronic heat capacities to be the same. Such extraneous heat capacity should be separated and evaluated by subtracting a normal portion of the heat capacity, which may be assumed to be approximately that of the non-magnetic compound of $YBa_2Cu_3O_{7-\delta}$. An estimation reported by Ferreira et al. [90] is shown in Fig. 9, where a tentative energy-level scheme is given. However, their heat capacity values were obtained by using a semiadiabatic calorimeter. A comparison of the heat capacity data is given for M ≡ Tm or Ho in Fig. 10, where reliable accurate data obtained by adiabatic calorimetry [45,46] are given together with the data of Ferreira et al. [90], indicating large discrepancies between them. Although extensive investigations into this phenomenon have been undertaken [88,91–93], very few reliable data are available for heat capacities measured in the wide temperature region from liquid helium temperature up to room temperature [43–47,94]. This is the reason why accurate data are so important.

FLUCTUATION PHENOMENA

The observation of fluctuation effects has been predicted in the heat capacity curve at T_c of a well-synthesized sample of $YBa_2Cu_3O_{7-\delta}$ because of the short coherent length, according to Ginzburg–Landau theory. Such bulk Gaussian fluctuations were first observed by Inderhees et al. [95] and Muzikar [96], as shown in Fig. 11. Some deviation from BCS-type anomaly can be seen, which is of a typical second-order phase transition with a heat capacity jump at T_c. The curve was fitted on the basis of 3-dimensional Gaussian fluctuations, and the number of order-parameter components is estimated as 7 ± 2 from the amplitudes. Such studies have been extended to

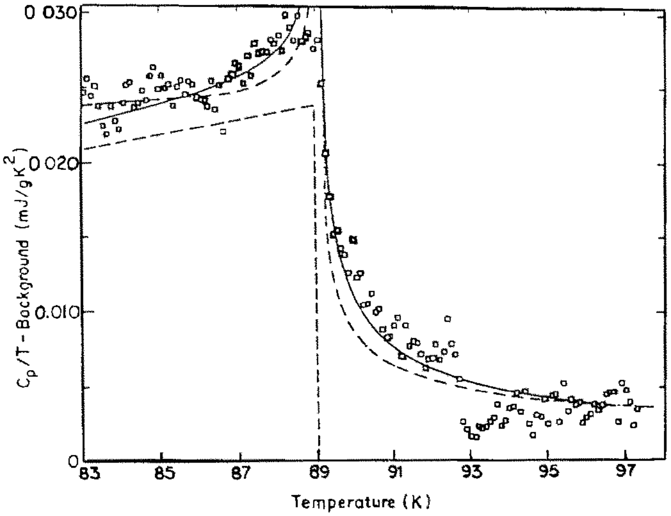

Fig. 11. Excess heat capacities due to the superconducting phase transition of YBa$_2$Cu$_3$O$_{7-\delta}$. — — —, BCS-type contribution; ———, sum of the BCS-type part and the 3-dimensional Gaussian fluctuation contribution; ·—·—· the best fit for the 2-dimensional contribution (different background included) [95].

measurements under magnetic fields [97,98]. Some theoretical studies have been made [99–103]. Experimentally, fluctuation phenomena have been observed also in electrical conductivity, magnetic susceptibility and thermopower, and studied in detail.

For the Bi-type compound, fluctuation effects have been observed by Okazaki et al. [104]. The heat capacity curve was analyzed in detail, and the 2-dimensionality was pointed out for the fluctuation effect, with a coherent length of 13 Å in the plane.

THERMODYNAMIC FUNCTIONS

Heat capacity itself is a useful value in the study of thermodynamic properties. The standard thermodynamic functions such as enthalpy, entropy and Gibbs energy can be obtained by intergrating some values derived from the heat capacities, which thus should be measured accurately for a wide temperature region from liquid helium temperatures up to room temperature. However, only a few reports have been accompanied by data for absolute values of the heat capacities of high-T_c oxide superconductors [45–47,56].

Further information is deduced from heat capacities, for example concerning phonon density of states in the solids [13], hopefully in comparison with the calculated values obtained on the basis of lattice dynamics [105–

107]. The excess heat capacities due to the superconducting phase transition must be estimated by subtracting the normal portion [108]. Recently, an attempt has been reported for such kinds of study by Gordon et al. [109], who have also pointed out the appearance of fluctuation effects. Experimental and theoretical supports are strongly required to develop the investigations [110–120].

The oxygen deficiency effect is also a very interesting aspect of high-T_c oxide superconductors. The heat capacities have been studied in order to observe such phenomena of nonstoichiometry [29,61,66,67]. Critical evidence of superconducting phase transition has been provided for a sample of the orthorhombic II phase of $YBa_2Cu_3O_{6.6}$ with $T_c \approx 60$ K by detecting a heat capacity anomaly using a high-precision adiabatic calorimeter [121].

HEAT CAPACITIES UNDER MAGNETIC FIELDS

It is also fruitful to measure heat capacities under various external fields: high pressures, magnetic fields, and so on. Some studies have been carried out in order to observe the effects of magnetic fields [67,97,98,122–126]. At low temperatures, the linear term problem has been studied under magnetic fields, which exert little influence on the La–M–Cu–O series of compounds with T_c below 40 K, and the applicability of the resonating-valence-bond model has been inspected [67,122]. In the case of compounds of the $YBa_2Cu_3O_{7-\delta}$ group, the heat capacities under various magnetic fields have been analyzed to obtain the crystal field contributions and to estimate the values of gJ [122–124]. The critical exponents of the heat capacity anomaly at T_c have been studied under magnetic fields [97,98,125]. Recently, the studies have been extended also to the Bi-type compound [126].

CONCLUDING REMARKS

More recently, thermodynamic studies have been extended to newly found compounds such as $K_{0.4}Ba_{0.6}BiO_3$ [127] and $MBa_2Cu_4O_8$ (where M ≡ rare earth elements) [128]. Much information is expected to be deduced from the heat capacities, and detailed analyses can be realized only on the basis of precise and reliable data. However, such reports have been very few so far. Accurate measurements are strongly required for high quality samples, and this is the first step in this field of investigation.

REFERENCES

1 J.G. Bednorz and K.A. Müller, Z. Phys. B, 64 (1986) 189.
2 L.E. Wenger, J.T. Chen, G.W. Hunter and E.M. Logothetis, Phys. Rev. B, 35 (1987) 7213.

3 M.E. Reeves, T.A. Friedmann and D.M. Ginsberg, Phys. Rev. B, 35 (1987) 7207.

4 M.B. Maple, K.N. Yang, M.S. Torikachvili, J.M. Ferreira, J.J. Neumeier, H. Zhou, Y. Dalichaouch and B.W. Lee, Solid State Commun., 63 (1987) 635.

5 E. Zirngiebl, J.O. Willis, J.D. Thompson, C.Y. Huang, J.L. Smith, Z. Fisk, P.H. Hor, R.L. Meng, C.W. Chu and M.K. Wu, Solid State Commun., 63 (1987) 721.

6 Y. Maeno, Y. Aoki, H. Kamimura, J. Sakurai and T. Fujita, Jpn. J. Appl. Phys., 26 (1987) L402.

7 M. Decroux, A. Junod, A. Bezinge, D. Cattani, J. Cors, J.L. Jorda, A. Stettler, M. François, K. Yvon, Ø. Fischer and J. Muller, Europhys. Lett., 3 (1987) 1035.

8 K. Kitazawa, M. Sakai, S. Uchida, H. Takagi, K. Kishio, S. Kanbe, S. Tanaka and K. Fueki, Jpn. J. Appl. Phys., 26 (1987) L342.

9 K. Kitazawa, T. Atake, M. Sakai, S. Uchida, H. Takagi, K. Kishio, T. Hasegawa, K. Fueki, Y. Saito and S. Tanaka, Jpn. J. Appl. Phys., 26 (1987) L751.

10 Y. Saito and T. Atake, Rep. Res. Lab. Eng. Mater., Tokyo Inst. Technol., 13 (1988) 13.

11 B. Batlogg, A.P. Ramirez, R.J. Cava, R.B. van Dover and E.A. Rietman, Phys. Rev. B, 35 (1987) 5340.

12 B.D. Dunlap, M.V. Nevitt, M. Slaski, T.E. Klippert, Z. Sungaila, A.G. McKale, D.W. Capone, R.B. Poeppel and B.K. Flandermeyer, Phys. Rev. B, 35 (1987) 7210.

13 A.P. Ramirez, B. Batlogg, G. Aeppli, R.J. Cava, E. Rietman, A. Goldman and G. Shirane, Phys. Rev. B, 35 (1987) 8833.

14 G. Nieva, E.N. Martinez, F. de la Cruz, D.A. Esparza and C.A. D'Ovidio, Phys. Rev. B, 36 (1987) 8780.

15 M.K. Wu, J.R. Ashburn, C.J. Torng, P.H. Hor, R.L. Meng, L. Gao, Z.J. Huang, Y.Q. Wang and C.W. Chu, Phys. Rev. Lett., 59 (1987) 908.

16 Z.X. Zhao, L.Q. Chen, Q.S. Yang, Y.Z. Huang, G.H. Chen, R.M. Tang, G.R. Liu, C.G. Cui, L. Chen, L.Z. Wang, S.Q. Guo, L.S. Li and J.Q. Bi, Kexue Tongbao, 33 (1987) 661.

17 S. Hikami, T. Hirai and S. Kagoshima, Jpn. J. Appl. Phys., 26 (1987) L314.

18 A. Junod, A. Bezinge, T. Graf, J.L. Jorda, J. Muller, L. Antognazza, D. Cattani, J. Cors, M. Decroux, Ø. Fischer, M. Banovski, P. Genoud, L. Hoffmann, A.A. Manuel, M. Peter, E. Walker, M. François and K. Yvon, Europhys. Lett., 4 (1987) 247, 637.

19 K. Kitazawa, T. Atake, H. Ishii, H. Sato, H. Takagi, S. Uchida, Y. Saito, K. Fueki and S. Tanaka, Jpn. J. Appl. Phys., 26 (1987) L748.

20 H.F. Fischer, Cornell University, personal communication.

21 F. Li, Q. Li, G. Lu, K. Wu, Y. Zhou, C. Li and D. Yin, Solid State Commun., 64 (1987) 209.

22 M.V. Nevitt, G.W. Crabtree and T.E. Klippert, Phys. Rev. B, 36 (1987) 2398.

23 S.E. Inderhees, M.B. Salamon, T.A. Friedmann and D.M. Ginsberg, Phys. Rev. B, 36 (1987) 2401.

24 C. Ayache, B. Barbara, E. Bonjour, R. Calemczuk, M. Couach, J.H. Henry and J. Rossat-Mignod, Solid State Commun., 64 (1987) 247.

25 Z. Chen, Y. Zhao, H. Yang, Z. Chen, D. Zheng, Y. Qian, B. Wu, Q. Zhang, Solid State Commun., 64 (1987) 685.

26 R. Shaviv, E.F. Westrum, Jr., M. Sayer, X. Yu, R.J.C. Brown, R.D. Heyding and R.D. Weir, J. Chem. Phys., 87 (1987) 5040.

27 M.B. Salamon and J. Bardeen, Phys. Rev. Lett., 59 (1987) 2615.

28 J.C. van Miltenburg, A. Schuijff, K. Kadowaki, M. van Sprang, J.Q.A. Koster, Y.K. Huang, A.A. Menovsky and H. Barten, Physica B, 146 (1987) 319.

29 C.S. Jee, T. Yuen, J.E Crow, C.L. Lin, P. Schlottmann, G.H. Myer and N. Bykovetz, Rev. Solid State Sci., 1 (1987) 279.

30 A. Junod, A. Bezinge, D. Cattani, J. Cors, M. Decroux, Ø. Fischer, P. Genoud, L. Hoffmann, J.L. Jorda, J. Muller and E. Walker, Jpn. J. Appl. Phys., Suppl., 26(3) (1987) 1119.

31 J. Blezius and J.P. Carbotte, Phys. Rev. B, 36 (1987) 3622.
32 M. Schossmann, F. Marsiglio and J.P. Carbotte, Phys. Rev. B, 36 (1987) 3627.
33 J. Heremans, D.T. Morelli, G.W. Smith and S.C. Strite III, Phys. Rev. B, 37 (1988) 1604.
34 R. Akis, F. Marsiglio and J.P. Carbotte, Phys. Rev. B, 39 (1989) 2722.
35 A. Junod, A. Bezinge and J. Muller, Physica C, 152 (1988) 50.
36 A. Junod, A. Bezinge, D. Eckert, T. Graf and J. Muller, Physica C, 152 (1988) 495.
37 R.A. Butera, Phys. Rev. B, 37 (1988) 5909.
38 M. Ishikawa, Y. Nakazawa, T. Takabatake, A. Kishi, R. Kato and A. Maesono, Solid State Commun., 66 (1988) 201.
39 H.M. Ledbetter and S.A. Kim, Phys. Rev. B, 38 (1988) 11857.
40 T. Laegreid and K. Fossheim, Europhys. Lett., 6 (1988) 81.
41 K. Kishio, O. Nakamura, K. Kuwahara, K. Kitazawa and K. Fueki, Jpn. J. Appl. Phys., 26 (1987) L694.
42 T.J. Kistenmacher, Solid State Commun., 65 (1988) 981.
43 Y. Saito, T. Nakamura and T. Atake, Mater. Res. Soc. Symp. Proc., 99 (1988) 475.
44 T. Atake, Y. Takagi, T. Nakamura and Y. Saito, Phys. Rev. B, 37 (1988) 552.
45 T. Atake, H. Kawaji, S. Takanabe, Y. Saito, K. Mori and Y. Saeki, Thermochim. Acta, 139 (1989) 169.
46 T. Atake, Q.Z. Zhang, Y. Takagi and Y. Saito, Rep. Res. Lab. Eng. Mater., Tokyo Inst. Technol., 14 (1989) 11.
47 T. Atake, Internat. Symp. on Superconductivity and Ionic Character in Layered Compounds, Tokyo Inst. Technol., 13–14 November 1989, Abstracts (1989) 37.
48 Y.P. Feng, A. Jin, D. Finotello, K.A. Gillis, M.H.W. Chan and J.E. Greedan, Phys. Rev. B, 38 (1988) 7041.
49 N. Wada, H. Muro-oka, Y. Nakamura and K. Kumagai, Physica C, 157 (1989) 453.
50 M.E. Reeves, D.S. Citrin, B.G. Pazol, T.A. Friedmann and D.M. Ginsberg, Phys. Rev. B, 36 (1987) 6915.
51 Z. Chen, H. Liu, Z. Mao, K. Wang, X. Zhan and Y. Zhang, Physica C, 156 (1988) 834.
52 R.A. Fisher, S. Kim, S.E. Lacy, N.E. Phillips, D.E. Morris, A.G. Markelz, J.Y.T. Wei and D.S. Ginley, Phys. Rev. B, 38 (1988) 11942.
53 D.N. Zheng, H.S. Yang, Z.J. Chen, J.H. Wang, Y.F. Yan, Y.M. Ni, G.H. Chen, K.Q. Wang, S.L. Jia and Z.X. Zhao, Modern Phys. Lett. B, 3 (1989) 163.
54 F. Seidler, P. Böhm, H. Geus, W. Braunisch, E. Braun, W. Schnelle, Z. Drzazga, N. Wild, B. Roden, H. Schmidt, D. Wohlleben, I. Felner and Y. Wolfus, Physica C, 157 (1989) 375.
55 R. Jin, F. Shi, Q. Ran, N. Shi, Z. Shi and S. Zhou, Physica C, 158 (1989) 255.
56 T. Atake, H. Kawaji, M. Itoh, T. Nakamura and Y. Saito, Physica C, 162 (1989) 488.
57 S.J. Collocott, G.K. White, S.X. Dou and R.K. Williams, Phys. Rev. B, 36 (1987) 5684.
58 M. Kato, Y. Maeno and T. Fujita, Physica C, 152 (1988) 116.
59 K. Kumagai, Y. Nakamichi, I. Watanabe, Y. Nakamura, H. Nakajima, N. Wada and P. Lederer, Phys. Rev. Lett., 60 (1988) 724.
60 L.R. Testardi, W.G. Moulton, H. Mathias, H.K. Ng, C.M. Rey and R.J. Kennedy, Phys. Rev. B, 36 (1987) 8816.
61 C. Ayache, B. Barbara, E. Bonjour, P. Burlet, R. Calemczuk, M. Couach, M.J.G.M. Jurgens, J.Y. Henry and J. Rossat-Mignod, Physica, 148B (1987) 305.
62 S.J. Collocott, R. Driver, L. Dale and S.X. Dou, Phys. Rev. B, 37 (1988) 7917.
63 S. von Milnár, A. Torressen, D. Kaiser, F. Holtzberg and T. Penney, Phys. Rev. B, 37 (1988) 3762.
64 R. Kuentzler, Y. Dossmann, S. Vilminot and S. El Hadigui, Solid State Commun., 65 (1988) 1529.
65 S. Vieira, S. Bourgeal, R. Villar, A. Aguilo and M.A. Ramos, Solid State Commun., 65 (1988) 1555.

66 R.J. Cava, B. Batlogg, A.P. Ramirez, D. Werder, C.H. Chen, E.A. Rietman and S.M. Zahurak, Mater. Res. Soc. Symp. Proc., 99 (1988) 19.

67 A.P. Ramirez, R.J. Cava, G.P. Espinosa, J.P. Remeika, B. Batlogg, S. Zahurak and E.A. Rietman, Mater. Rev. Soc. Symp. Proc., 99 (1988) 459.

68 S.J. Collocott, R. Driver, H.K. Welsh and C. Andrikidis, Physica C, 152 (1988) 401.

69 D. Eckert, A. Junod, A. Bezinge, T. Graf and J. Muller, J. Low Temp. Phys., 73 (1988) 241.

70 B. Golding, N.O. Birge, W.H. Haemmerle, R.J. Cava and E. Rietman, Phys. Rev. B, 36 (1987) 5606.

71 I. Felner, Y. Wolfus, G. Hilscher and N. Pillmayr, Phys. Rev. B, 39 (1989) 225.

72 M. Sera, S. Kondoh, K. Fukuda and M. Sato, Solid State Commun., 66 (1988) 1101.

73 K. Kumagai and Y. Nakamura, Physica C, 152 (1988) 286.

74 S.J. Collocott, R. Driver, C. Andrikidis and F. Pavese, Physica C, 156 (1988) 292.

75 J.O. Willis, Z. Fisk, J.D. Thompson, S.-W. Cheong, R.M. Aikin, J.L. Smith and E. Zirngiebl, J. Magn. Magn. Mater., 67 (1987) L139.

76 J.C. Ho, P.H. Hor, R.L. Meng, C.W. Chu and C.Y. Huang, Solid State Commun., 63 (1987) 711.

77 S.E. Brown, J.D. Thompson, J.O. Willis, R.M. Aikin, E. Zirngiebl, J.L. Smith, Z. Fisk and R.B. Schwarz, Phys. Rev. B, 36 (1987) 2298.

78 S.H. Bloom, M.V. Kuric, R.P. Guertin, C. Jee, D. Nichols, E. Kaczanowicz, J.E. Crow, G. Myer and R.E. Salomon, J. Magn. Magn. Mater., 68 (1987) L135.

79 B.D. Dunlap, M. Slaski, D.G. Hinks, L. Soderholm, M. Beno, K. Zhang, C. Segre, G.W. Crabtree, W.K. Kwok, S.K. Malik, Ivan K. Schuller, J.D. Jorgensen and Z. Sungaila, J. Magn. Magn. Mater., 68 (1987) L139.

80 J. van den Berg, C.J. van der Beek, P.H. Kes, J.A. Mydosh, G.J. Niewenhuys and L.J. de Jongh, Solid State Commun., 64 (1987) 699.

81 A.P. Ramirez, L.F. Schneemeyer and J.V. Waszczak, Phys. Rev. B, 36 (1987) 7145.

82 Y. Nakazawa, M. Ishikawa and T. Takabatake, Physica, 148B (1987) 404.

83 B.D. Dunlap, M. Slaski, Z. Sungaila, D.G. Hinks, K. Zhang, C. Segre, S.K. Malik and E.E. Alp, Phys. Rev. B, 37 (1988) 592.

84 M.W. Dirken and L.J. de Jongh, Solid State Commun., 64 (1987) 1201.

85 S. Simizu, S.A. Friedberg, E.A. Hayri and M. Greenblatt, Phys. Rev. B, 36 (1987) 7129.

86 B.W. Lee, J.M. Ferreira, Y. Dalichaouch, M.S. Torikachvili, K.N. Yang and M.B. Maple, Phys. Rev. B, 37 (1988) 2368.

87 R.J. Cava, B. Batlogg, R.M. Fleming, S.A. Sunshine, A. Ramirez, E.A. Rietman, S.M. Zahurak and R.B. van Dover, Phys. Rev. B, 37 (1988) 5912.

88 M.T. Causa, C. Fainstein, G. Nieva, R. Sânchez, L.B. Steren, M. Tovar, R. Zysler, D.C. Vier, S. Schultz, S.B. Oseroff, Z. Fisk and J.L. Smith, Phys. Rev. B, 38 (1988) 257.

89 G. Zhao, R. Wang, H. Li, R. Qi-ze, Z. Chuan-xing, L. Li and W. Guan, Phys. Rev. B, 38 (1988) 5035.

90 J.M. Ferreira, B.W. Lee, Y. Dalichaouch, M.S. Torikachvili, K.N. Yang and M.B. Maple, Phys. Rev. B, 37 (1988) 1580.

91 A. Furrer, P. Brüesch and P. Unterbährer, Phys. Rev. B, 38 (1988) 4616.

92 N. Sankar, V. Sankaranarayanan, L.S. Vaidhyanathan, G. Rangarajan, R. Srinivasan, K.A. Thomas, U.V. Varadaraju and G.V. Subba Rao, Solid State Commun., 67 (1988) 391.

93 P. Allenspach, A. Furrer and F. Hulliger, Phys. Rev. B, 39 (1989) 2226.

94 T. Atake, H. Kawaji, A. Hamano and Y. Saito, Rep. Res. Lab. Eng. Mater., Tokyo Inst. Technol., 15 (1990) 13.

95 S.E. Inderhees, M.B. Salamon, N. Goldenfeld, J.P. Rice, B.G. Pazol, D.M. Ginsberg, J.Z. Liu, and G.W. Crabtree, Phys. Rev. Lett., 60 (1988) 1178.

96 P. Muzikar, Phys. Rev. Lett., 61 (1988) 479.

97 M.B. Salamon, S.E. Inderhees, J.P. Rice, B.G. Pazol, D.M. Ginsberg and N. Goldenfeld, Phys. Rev. B, 38 (1988) 885.
98 S.E. Inderheers and M.B. Salamon, Modern Phys. Lett. B, 3 (1989) 111.
99 A. Kapitulnik, M.R. Beasley, C. Castellani and C. Di Castro, Phys. Rev. B, 37 (1988) 537.
100 L. Tewordt, D. Fay and Th. Wölkhausen, Solid State Commun., 67 (1988) 301.
101 J.F. Annett, M. Randeria and S.R. Renn, Phys. Rev. B, 38 (1988) 4660.
102 K.F. Quader and E. Abrahams, Phys. Rev. B, 38 (1988) 11977.
103 C.T. Rieck, Th. Wölkhausen, D. Fay and L. Tewordt, Phys. Rev. B, 39 (1989) 278.
104 N. Okazaki, T. Hasegawa, K. Kishio, K. Kitazawa, A. Kishi, Y. Ikeda, M. Takano, K. Oda, H. Kitaguchi, J. Takada and Y. Miura, Phys. Rev. B, 41 (1990) 4296.
105 J. Prade, A.D. Kulkarni, F.W. de Wette, W. Kress, M. Cardona, R. Reiger and U. Schröder, Solid State Commun., 64 (1987) 1267.
106 W. Kress, U. Schröder, J. Prade, A.D. Kulkarni and F.W. de Wette, Phys. Rev. B, 38 (1988) 2906.
107 S. Mase and T. Yasuda, Solid State Commun., 68 (1988) 655.
108 O. Beckman, L. Lundgren, P. Nordblad, L. Sandlund, P. Svedlindh, T. Lundström and S. Rundqvist, Phys. Lett. A, 125 (1987) 425.
109 J.E. Gordon, M.L. Tan, R.A. Fisher and N.E. Phillips, Solid State Commun., 69 (1989) 625.
110 A.E. Ruckenstein, P.J. Hirschfeld and J. Appel, Phys. Rev. B, 36 (1987) 857.
111 X. Chen and S. Chen, Solid State Commun., 65 (1988) 873.
112 R. Combescot, Phys. Rev. B, 37 (1988) 2235.
113 J.I. Gersten, Phys. Rev. B, 37 (1988) 3366.
114 T. Datta, H.M. Ledbetter, C.E. Violet, C. Almasan and J. Estrada, Phys. Rev. B, 37 (1988) 7502.
115 G.K. White, S.J. Collocott, R. Driver, R.B. Roberts and A.M. Stewart, J. Phys. C, 21 (1988) L631.
116 Y. He, S. Lin, B. Zhang, J. Xiang, W. Cui, Y. Li, J. Zhang, C. Lin, J. Li, C. Li and D. Yin, J. Phys. C, 21 (1988) L783.
117 K.S. Athreya, O.B. Hyun, J.E. Ostenson, J.R. Clem and D.K. Finnenmore, Phys. Rev. B, 38 (1988) 11846.
118 S.L. Cooper, F. Slakey, M.V. Klein, J.P. Rice, E.D. Bukowski and D.M. Ginsberg, Phys. Rev. B, 38 (1988) 11934.
119 R. Akis and J.P. Carbotte, Physica C, 157 (1989) 395.
120 V.Z. Kresin and S.A. Wolf, Physica C, 158 (1989) 76.
121 T. Atake, S. Takanabe, H. Kawaji and Y. Saito (in preparation).
122 N.E. Phillips, R.A. Fisher, S.E. Lacy, C. Marcenat, J.A. Olsen, W.K. Ham, A.M. Stacy, J.E. Gordon and M.L. Tan, Physica B, 148 (1987) 360.
123 H.P. van der Meulen, J.J.M. Franse, Z. Tarnawski, K. Kadowaki, J.C.P. Klaasse and A.A. Menovsky, Physica C, 152 (1988) 65.
124 T. Sasaki, O. Nakatsu, N. Kobayashi, A. Tokiwa, M. Kikuchi, A. Liu, K. Hiraga, Y. Syono and Y. Muto, Physica C, 156 (1988) 395.
125 C. Ebner and D. Stroud, Phys. Rev. B, 39 (1989) 789.
126 R. Caspary, A. Höhr, H. Spille, F. Steglich, H. Schmidt, R. Ahrens, G. Roth, H. Rietschel, Y.F. Yan and Z.X. Zhao, Europhys. Lett., 8 (1989) 639.
127 J.E. Graebner, L.F. Schneemeyer and J.K. Thomas, Phys. Rev. B, 39 (1989) 9682.
128 R.M. Hazen, L.W. Finger and D.E. Morris, Appl. Phys. Lett., 54 (1989) 1057.