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Effect of Mn doping on the specific heat of the high T_C superconductor $REBa_2Cu_3O_y$ (RE = Y, Gd)

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Abstract
We present measurements of specific heat in Mn-doped compounds $REBa_2(Cu_{1-x}Mn_x)_3O_y$ (RE = Y and Gd) with $0 \leqslant x \leqslant 2\%$. It is found that the transition temperature of Mn-doped $YBa_2(Cu_{1-x}Mn_x)_3O_y$ (YBaCuMnO) compounds does not change appreciably. On the other hand, in the case of $GdBa_2(Cu_{1-x}Mn_x)_3O_y$ (GdBaCuMnO) samples, the transition temperature decreases noticeably with the increase in Mn concentration. In REBaCuMnO, a jump in specific heat at the superconducting transition was observed for a low concentration of Mn; however, only a small change in slope was noticed for Mn concentrations above 1%. Replacing 0.5% Cu by Mn has only a marginal effect on the transition temperature, but a three-fold suppression of the specific heat jump is observed with such a substitution. This finding clearly demonstrates that these constituents are being incorporated into the superconductors as a whole and not in the form of a local cluster.

1. Introduction

There have been numerous efforts to discover new superconducting materials while seeking to explain the transport mechanism in ceramic high temperature superconductors. Nevertheless, a complete understanding of the underlying principles behind the superconductivity is still elusive, especially in high temperature superconductors. Several investigators have carried out substitution experiments in high T_C superconductors, which has helped further understanding of the mechanism of superconductivity as well as improving the magnetic properties, like flux pinning etc, in order to enhance the applicability of these materials. In particular, substituting transition metal elements, for example Zn, Fe, Ni and Co, for Cu dramatically affects the superconducting and normal state properties [1–8]. Different impurities have preferential occupancies due to the presence of two copper sites in these high T_C superconductors, a plane and a chain. Dopants like Fe and Co occupy plane sites with an accompanying orthorhombic to tetragonal structural transformation [1–3]. However no such transformation is observed for Zn and Ni that occupy chain sites [4–8]. The structural transformation leads to corresponding variations in the physical properties, such as the lattice components of specific heat, the coefficient of thermal expansion and the pressure dependence of the transition temperature, dT_C/dP.

A vast number of investigations have been reported in the literature on measurements of specific heat in pure and doped REBCO compounds [9–19]; however, relatively less work has been done on substitution of Mn, possibly owing to the low solubility of Mn. Such an investigation is of great importance from the theoretical point of view, due to some features in common between various transition metal ions. In particular, Mn doping shows unusual behaviour in the way that the transition temperature of $YBa_2Cu_3O_y$ is only slightly affected by the Mn content [20–22], while significant depression of T_C was observed with Fe, Co and Ni substitution for Cu. In fact, Mn behaves like Fe or Co [23, 24] as far as the occupancy of copper plane site is concerned; while it behaves like Zn or Ni as far as the retention of orthorhombicity is concerned [25]. Nishida *et al* [26] carried our electron spin resonance (ESR) studies of Mn-doped samples of $YBa_2Cu_3O_y$ with Mn substitution up to 10%. They have suggested a Korringa type interaction between Mn localized moments and Cu spins. Samuel *et al* [20] carried out a dc magnetization study of Mn-doped $YBa_2Cu_3O_y$ and found that 5% Mn reduces the transition temperature by 1.9 K, which is considerably lower than that found by others [21–27]. In order to clarify the role of Mn substitution in the high T_C superconductors, we present a systematic study of the specific heat of YBaCuMnO and GdBaCuMnO systems in the temperature range 65–300 K, with Mn substitution up to 2%.

2. Experimental techniques

All the samples of the $YBa_2(Cu_{1-x}Mn_x)_3O_y$ system in the nominal doping range $0 \leqslant x \leqslant 2\%$ were prepared by the standard solid-state reaction route. High purity (>99.99%) Y_2O_3, (Gd_2O_3), $BaCO_3$,CuO and MnO were thoroughly mixed in an agate mortar and then calcined at 930 °C in air for 12 h. The mixing and calcination was repeated three times to improve the homogeneity. The powder was cold pressed into pellets, followed by annealing at 930 °C under an oxygen atmosphere for 72 h. This was followed by a slow cooling to 450 °C and maintenance at this temperature for about 6 h. The x-ray diffraction technique was used to determine the atomic spacing of the superconducting compounds and to see if any impurity phases are present. All the samples prepared in the present investigation are single-phased. The unit cell parameters show that all the samples remain orthorhombic. This is in good agreement with the observations of Kallias *et al* [25]. The resistivity measurements were performed with a standard four-probe method, using Ag paste as the contact with an alternating current source, which discards thermoelectric effects.

Relative specific heats were measured with a high-resolution ac calorimeter, using chopped light as a heat source. Photoabsorbing PbS film was evaporated on samples, which were sanded to a thickness of about 0.2 mm to ensure 'one-dimensional' heat flow. The averaged and oscillating temperatures (T_{ac}) of the sample were detected by an E-type thermocouple of 25 μm in diameter, attached with small amount of GE varnish. The frequency dependence of T_{ac} was measured at various temperatures to determine the correct range of chopping frequencies. For an appropriately chosen chopping frequency (typically 2–12 Hz), the magnitude of the temperature oscillation is inversely proportional to the total heat capacity (including the sample and addendum). Notice that the ac technique does not give the absolute value of specific heat without detailed knowledge of the power absorbed from the light pulse. The absolute values of the molar heat capacity for the samples were obtained by normalizing the ac data to the

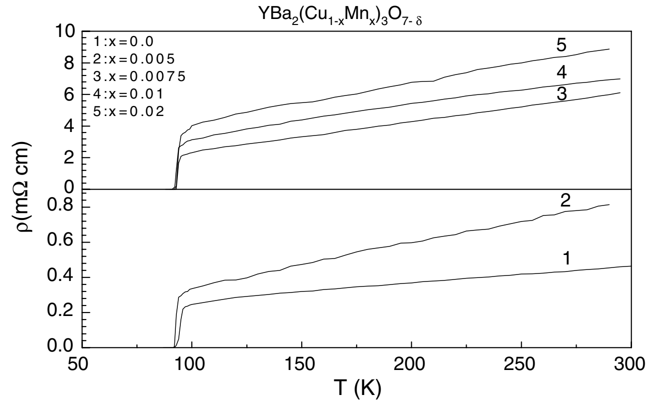

Figure 1. Resistivity versus temperature plots of the samples $YBa_2(Cu_{1-x}Mn_x)_3O_y$ for various values of x.

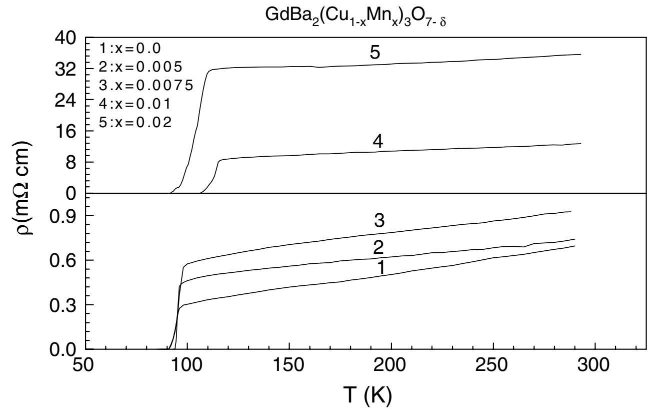

Figure 2. Resistivity versus temperature plots of $GdBa_2(Cu_{1-x}Mn_x)_3O_y$ for various samples (1, 2, 3, 4, 5 denotes $x = 0$, 0.5, 0.75, 1, 2%, respectively).

published result at 300 K. Here we assume that the REBCO with the same chemical formula and crystal structure should possess a comparable molar heat capacity at high temperatures.

3. Results and discussion

We present the resistivity versus temperature data for YBaCuMnO samples in figure 1. All the superconducting samples show a metallic behaviour in the normal state. Resistivity increases monotonically with the dopant concentration; however, for the sample with $x = 0.75\%$, there is a 10-fold increase in resistivity which is possibly due to the fact that Mn induces strong fluctuations near the transition temperature. The transition widths in these compounds lie in the range 1–3 K. The electrical resistivities of the samples in the present investigations are in good agreement with that in literature. To compare the results, the resistivity of sample with $x = 0.5\%$ at 100 K is 3×10^{-4} Ω cm whereas that observed by Samuel *et al* [20] is about 2×10^{-4} Ω cm.

The resistivity values for the GdBaCuMnO samples are shown in figure 2. All the samples show metallic behaviour in the normal state and the resistivity increases monotonically

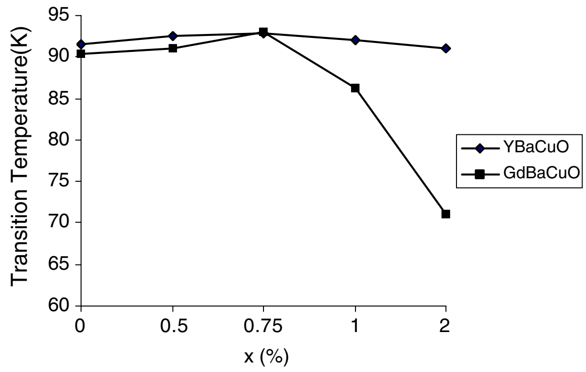

Figure 3. Variation of transition temperature for YBaCuMnO and GdBaCuMnO compounds with Mn concentration.

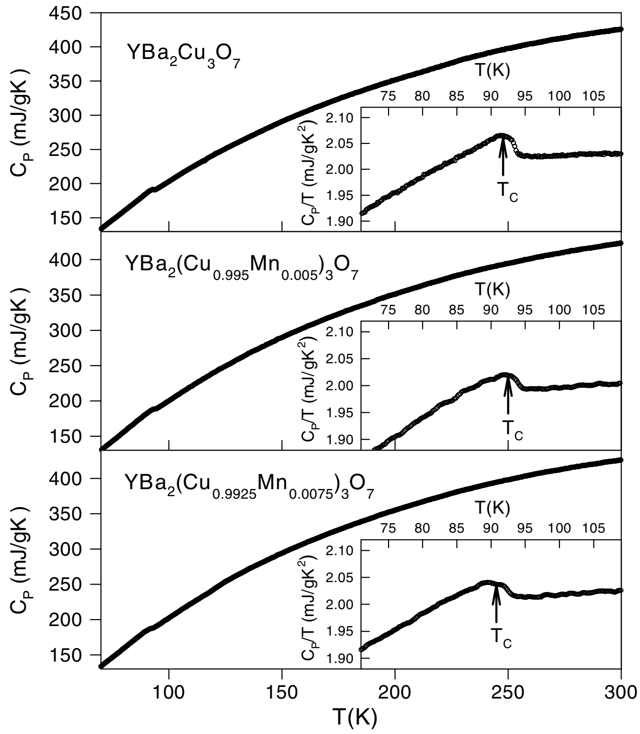

Figure 4. The temperature dependence of specific heat of pure and Mn-doped YBaCuO samples with $x = 0.5\%$ and 0.75%. The insets shows temperature dependent variations of C_P/T in the vicinity of the transition temperature. A specific heat jump was observed in all these samples.

with dopant concentration. Similar to YBaCuMnO samples, a drastic increase in resistivity is observed for the sample with $x = 1\%$ which is also due to the fact that Mn induces strong fluctuations near the transition temperature. Figure 3 shows the variation of onset of the transition temperature with Mn concentration for YBaCuMnO and GdBaCuMnO. It is evident that there is only a marginal change in transition temperature with the increase in Mn doping for YBaCuMnO compounds. This is in good agreement with the earlier reported

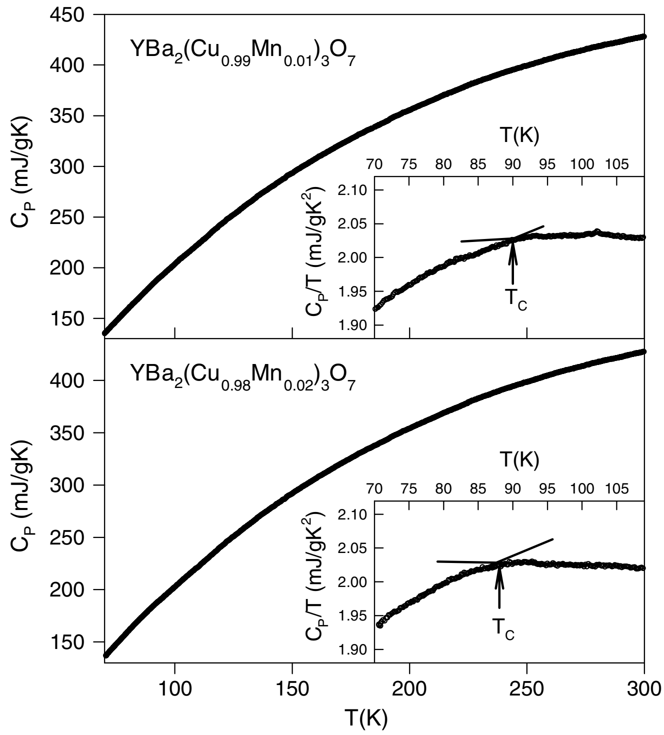

Figure 5. The temperature dependence of the specific heat of Mn-doped samples with $x = 1$ and 2%. The insets show temperature dependent variations of C_P/T in the vicinity of the transition temperature.

results [20]. Conversely, for GdBaCuMnO compounds there is a noticeable decrease in transition temperature with the increase in Mn concentration.

Figure 4 shows the temperature dependent specific heat of $YBa_2(Cu_{1-x}Mn_x)_3O_y$ ($0 \leqslant x \leqslant 0.75\%$) in the temperature range 65–300 K. In the insets, the specific heat data are depicted in the vicinity of transition temperature (T_C) of the respective samples. Here we have plotted C_P/T as a function of temperature. The anomaly at the transition temperature is clearly seen in all the samples. Although the value of T_C remains essentially unchanged, the specific heat jump decreases as the Mn concentration increases.

Figure 5 depicts the specific heat data of 1% and 2% Mn-doped samples in the temperature range 65–300 K. It is found that a change in slope can be noticed in the vicinity of T_C for those samples with a high Mn doping level, which is similar to the earlier reported results on other doped YBaCuO compounds [9–11]. This change in behaviour from 'clear peak' to 'change in slope' is possibly due to the drastic change in resistivity.

It is worth mentioning that the anomalies found in these samples cannot be described by traditional Bardeen–Cooper–Schrieffer (BCS) theory, where a broadening in the specific heat was observed. In the conventional superconductors, a sharp discontinuity is usually observed in the specific heat at the superconducting transition temperature. This difference in behaviour is due to the broad transition widths (about 2–3 K) in high T_C superconductors compared with the sharp widths (about 1 mK) in conventional superconductors. The jump in specific heat at T_C was determined by extrapolating the two branches of C_P/T versus T curves at T_C. We have plotted C_P/T instead of C_P in the vicinity of transition temperature because the jumps

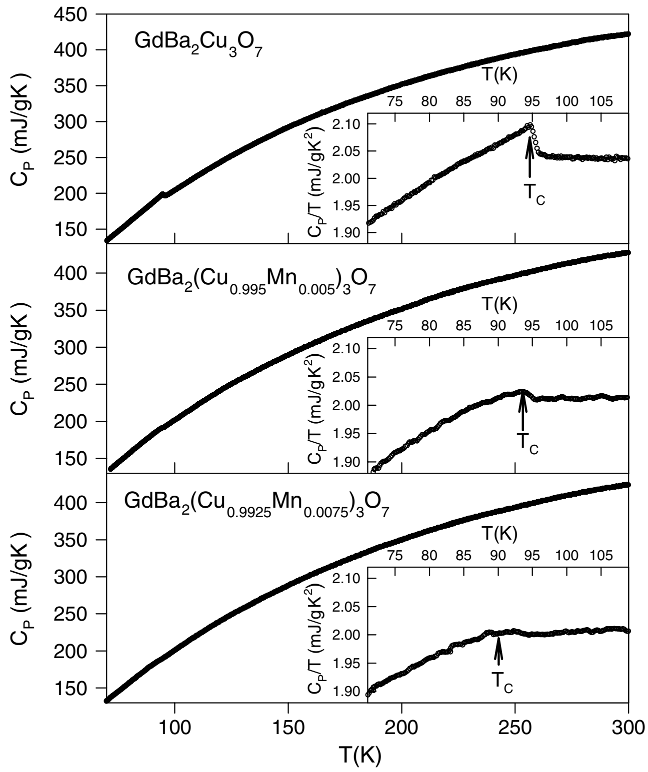

Figure 6. The temperature dependence of specific heat of pure and Mn-doped GdBaCuO samples with $x = 0.5\%$ and 0.75%. The insets shows temperature dependent variations of C_P/T in the vicinity of the transition temperature.

in specific heat are best seen in such plots, as shown in figures 4 and 5. For a pure YBaCuO sample, a jump of about 4.1 J mol^{-1} K^{-1} was observed, which is in good agreement with the observations of Sulkowski *et al* [18]. With a small amount of Mn doping of 0.5%, the jump decreases to 3.5 J mol^{-1} K^{-1}. As the doping level increases to 1%, there is no noticeable jump in specific heat, while only a change in slope is seen. This clearly demonstrates that these substituents are being incorporated into the superconductors as a whole and not in the form of a local cluster. If Mn were substituted in the form of a local cluster, then it would have no effect on the specific heat jump.

Figure 6 shows the temperature dependent specific heat of $GdBa_2(Cu_{1-x}Mn_x)_3O_y$ ($0 \leqslant x \leqslant 0.75\%$) in the temperature range 65–300 K. The insets shows temperature dependent variations of C_P/T in the vicinity of the transition temperature. The anomaly at the transition temperature is clearly seen in all the samples. However, no jump was observed for samples with Mn concentrations of more than 1% and only a change in slope was detected around the transition temperature. The change in behaviour from 'clear peak' to 'change in slope' is perhaps correlated with the drastic change in resistivity.

Similar to the YBaCuMnO system, the observed specific heat jump in these GdBaCuMnO compounds is rather broad. Using the method of extrapolation, the specific heat jump for the pure GdBaCuO sample is estimated to be about 5.7 J mol^{-1} K^{-1}, slightly larger than that of the YBaCuO sample. As observed in YBaCuMnO samples, the 0.5 and 0.75% Mn-doped samples of GdBaCuMn showed a jump in specific heat. However, for 1% and 2% doped samples of Mn

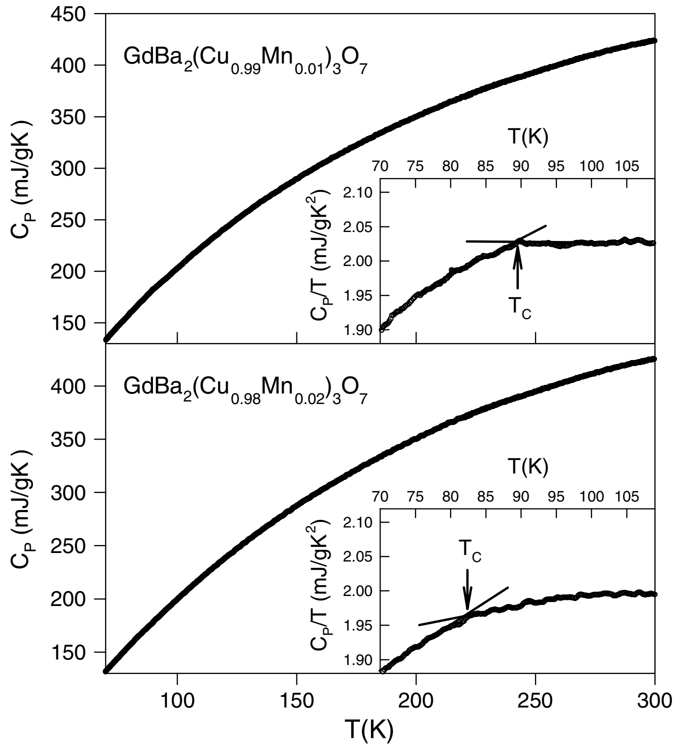

Figure 7. The temperature dependence of the specific heat of Mn-doped samples with $x = 1$ and 2%. The insets show temperature dependent variations of C_P/T in the vicinity of the transition temperature.

we could observe only a change in slope. This is shown in figure 7. Surprisingly, it is found that the specific heat jump decreases by almost a factor of 3 with only 0.5% Mn substitution for Cu, suggesting that Mn is being incorporated into the GdBaCuO system as a whole and not in the form of a local cluster.

4. Conclusions

In conclusion, detailed specific heat measurements were carried out on pure and Mn-doped samples of YBaCuO and GdBaCuO. The present results on the YBaCuMnO system show that the transition temperature remains almost unchanged with respect to Mn substitution. In contrast, there is a noticeable reduction in transition temperature in the GdBaCuMnO system. All the pure samples exhibit a clear jump in specific heat at the superconducting temperature. However, it is observed that a small amount of Mn substitution caused a strong suppression in the specific heat jump, suggesting that Mn is being incorporated into the REBaCuO system as a whole and not in the form of a local cluster.

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References

[1] Padalia B D, Gurman S J, Mehta P K and Prakash O 1992 *J. Phys.: Condens. Matter* **4** 6865
[2] Iwasaki H, Inaba S, Sugioka K, Nozaki Y and Kobayashi N 1997 *Physica* C **290** 113
[3] Akachi T, Escamilla R, Marquina V, Jimenez M, Marquina M L, Gomez R, Ridaura R and Aburto S 1998 *Physica* C **301** 315
[4] Nachumi B, Fudamoto Y, Keren A, Kojima K M, Larkin M, Luke G M, Merrin J, Tchernyshov O, Uemura Y J, Ichikawa N, Goto M and Uchida S 1997 *Physica* C **282–287** 1355
[5] Hussain M, Kuroda S and Takita K 1998 *Physica* C **297** 176
[6] Usagawa T, Utagawa T, Koyama S, Tanabe K and Shiohara Y 2002 *Physica* C **370** 132
[7] Rao A 1996 *J. Phys.: Condens. Matter* **8** 527
[8] Rao A 2004 *J. Phys.: Condens. Matter* **16** 1439
[9] Loram J W, Mirza K A, Freeman P F and Tallon J J 1991 *Supercond. Sci. Technol.* **4** S184
[10] Eagles D M 1993 *Physica* C **211** 319
[11] Mott N F 1992 *Physica* C **196** 369
[12] Haetinger C, Abergo Castillo I, Kunzler J V, Ghivelder L, Pureur P and Reich S 1996 *Supercond. Sci. Technol.* **9** 639
[13] Liang W Y, Loram J W, Mirza K A, Athanassopoulou N and Cooper J R 1996 *Physica* C **263** 277
[14] Dorbolo S, Houssa M and Ausloos M 1998 *Supercond. Sci. Technol.* **11** 76
[15] Marcenat C, Bouquet F, Calemczuk R, Welp U, Kwok W K, Crabtree G W, Phillips N E, Fisher R A and Schilling A 2000 *Physica* C **341** 949
[16] Junod A, Revaz B, Wang Y and Erb A 2000 *Physica* B **284–288** 1043
[17] Yang H D and Lin J-Y 2001 *J. Phys. Chem. Solids* **62** 1861
[18] Sulkowski C, Wlosewicz D, Matusiak M, Plackowski T, Sikora A and Horyn R 2003 *Physica* C **387** 187
[19] Lortz R, Junod A, Jaccard D, Wang Y, Meingast C, Masui T and Tajima S 2005 *J. Phys.: Condens. Matter* **17** 4135
[20] Isaac Samuel E, Seshu Bai V, Harish Kumar N and Malik S K 2001 *Supercond. Sci. Technol.* **14** 429
[21] Pop A V, Gh Ilonca, Ciurchea D, Al Darabont, Borodi G, Pop V and Giurgiu LV 1995 *J. Alloys Compounds* **223** 56
[22] Hien T D, Anh T H and Hoang N V 1992 *Phys. Status Solidi* a **131** K47
[23] Yang Y, Zhang B, Zhou H, Ding Y, Jin L, Yang C, Zha Y and Yuan W 1989 *Solid State Commun.* **70** 919
[24] Saini N L, Garg K B, Rajagopal H and Sequeira A 1992 *Solid State Commun.* **82** 895
[25] Kallias G and Niarchos D 1992 *Supercond. Sci. Technol.* **5** 56
[26] Nishida A, Taka C and Horai K 1998 *Adv. Supercond.* **10** 187
[27] Rao A, Radheshyam S, Das A, Agarwal S K, Lin Y K, Sivakumar K M and Kuo Y-K 2006 *J. Phys.: Condens. Matter* communicated