RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 50, NUMBER 13 1 OCTOBER 1994-I

Absence of a second antiferromagnetic transition in pure $YBa_2Cu_3O_{6+x}$

H. Casalta and P. Schleger
Risø National Laboratory, Department of Solid State Physics, P.O. Box 49, DK-4000 Roskilde, Denmark

E. Brecht
Technische Hochschule Darmstadt, Fachbereich Materialwissenschaft, Strukturforschung, D-64287 Darmstadt, Germany

W. Montfrooij, N. H. Andersen, and B. Lebech
Risø National Laboratory, Department of Solid State Physics, P.O. Box 49, DK-4000 Roskilde, Denmark

W. W. Schmahl and H. Fuess
Technische Hochschule Darmstadt, Fachbereich Materialwissenschaft, Strukturforschung, D-64287 Darmstadt, Germany

Ruixing Liang and W. N. Hardy
The University of British Columbia, Department of Physics, Vancouver, British Columbia, Canada V6T 1Z1

Th. Wolf
Kernforschungszentrum Karlsruhe, Institut für Technische Physik, P.O. Box 3640, D-76021 Karlsruhe, Germany

(Received 20 May 1994)

Magnetic ordering has been investigated by means of neutron scattering in an $YBa_2Cu_3O_{6+x}$ single crystal prepared with two different oxygen concentrations, $x=0.1$ and $x=0.18$, and in an aluminum-doped $YBa_2(Cu_{3-y}Al_y)O_{6+x}$ crystal with $x=0.25$ and $y=0.14$. For the undoped crystal, a magnetic ordering transition was observed at $T_N=410$ K and 368 K (respectively for $x=0.1$ and $x=0.18$), but *no second magnetic transition* was found down to 2 K. In contrast, an antiferromagnetic reordering was observed for the aluminum-doped sample with a transition temperature $T_2=8$ K. This implies a high sensitivity of this second phase to impurities and indicates that the transition is not necessarily an intrinsic property of $YBa_2Cu_3O_{6+x}$.

Experimental results have been reported about the existence of a second antiferromagnetic transition at low temperature in $YBa_2Cu_3O_{6+x}$,[1,2] which conflict with other experiments where it was not observed.[3–5] Furthermore, this second phase has been observed in related compounds, where the chain site copper Cu(1) in the basal CuO_x plane is partly substituted by magnetic impurities like Co (Ref. 6), or Fe (Ref. 7). Since the magnetism is potentially relevant for superconductivity, it is important to resolve this controversy. Additionally, the magnetism of $YBa_2Cu_3O_{6+x}$ is intrinsically interesting as an example of a quasi-two-dimensional (2D) antiferromagnetic Heisenberg *bilayered* system with a weak *XY anisotropy*.[5,8] Because the nonmagnetic Al impurities substitute on the Cu(1) site,[9] we decided to study by neutron scattering the magnetic ordering in the two following systems: (1) a pure $YBa_2Cu_3O_{6+x}$ crystal prepared in a zirconia crucible with two different oxygen contents $x=0.1$ and $x=0.18$ (denoted, respectively, YBCO1 and YBCO2 throughout this paper), and (2) a crystal substituted with 14% aluminum $YBa_2(Cu_{3-y}Al_y)O_{6+x}$ (denoted Al-YBCO). We would like to recall that the first magnetic transition (T_N; Néel temperature) is associated with the occurrence of $(h+\frac{1}{2},k+\frac{1}{2},l)$ magnetic Bragg reflections (with h, k, and l integers) because the periodicity is doubled along the a and b directions compared to the nuclear cell. The second antiferromagnetic transition (T_2) corresponds to an additional doubling of the magnetic cell along the c axis; the associated reflections have $(h+\frac{1}{2},k+\frac{1}{2},l+\frac{1}{2})$ indices. For YBCO1 and YBCO2, we found a T_N of 410 K and 368 K, respectively, and *no evidence* for a T_2 (down to 2 K). In contrast, this second transition was indeed observed for the Al-doped sample with a temperature $T_2 \sim 8$ K. These results show the extreme sensitivity of this second magnetic transition to impurities located in the chains, and they suggest that the appearance of this second phase could be triggered by oxygen inhomogeneities or modified bonding arrangements caused by the presence of Al in the basal plane. Furthermore, many $YBa_2Cu_3O_{6+x}$ samples and related compounds have been prepared in alumina crucibles, leading to aluminum contamination. Therefore we believe that the present result is important for a global understanding of the magnetism in $YBa_2Cu_3O_{6+x}$ and related compounds. Finally, the analysis of the magnetic structure emphasizes the anisotropic character of the magnetic form factor due to the $3d_{x^2-y^2}$ shell of the Cu(2) planar site.[10]

The 49-mg single crystal of $YBa_2Cu_3O_{6+x}$ was grown by a flux method in yttria stabilized zirconia crucibles using starting materials of 99.999% purity[11] and exhibits very good physical qualities.[12] The 55-mg aluminum-doped $YBa_2(Cu_{3-y}Al_y)O_{6+x}$ crystal was grown from BaO-CuO flux in an Al_2O_3 crucible by the slow-cooling method[13] (at an oxygen pressure of 1 bar and cooling rate of 0.30 °C/hour). After the growth, the aluminum-doped crystal was additionally annealed in flowing oxygen in the temperature range from 600 °C to 390 °C for 500 hours. Both the pure YBCO1 and Al-doped Al-YBCO crystals were deoxygenated

0163-1829/94/50(13)/9688(4)/$06.00

TABLE I. Magnetic Bragg peaks intensities observed for YBCO1 ($\mu=0.55\mu_B$) on the triple-axis TAS1 at $T=4.2$ K and calculated from Eq. (1). A set of nuclear Bragg peaks was measured to deduce the overall scaling factor for the observed intensities.

hkl	Q	I_{obs}	I_{calc}
$\frac{1}{2}\frac{1}{2}0$	1.151	0.00	0.00
$\frac{1}{2}\frac{1}{2}1$	1.269	12.59	12.07
$\frac{1}{2}\frac{1}{2}2$	1.569	23.32	23.82
$\frac{1}{2}\frac{1}{2}3$	1.970	6.54	6.44
$\frac{1}{2}\frac{1}{2}4$	2.422	3.74	3.25
$\frac{1}{2}\frac{1}{2}5$	2.902	23.45	22.28
$\frac{1}{2}\frac{1}{2}6$	3.397	16.90	16.97
$\frac{3}{2}\frac{3}{2}1$	3.495	2.83	3.05
$\frac{3}{2}\frac{3}{2}2$	3.615	4.53	5.23
$\frac{3}{2}\frac{3}{2}3$	3.806	1.43	1.38

simultaneously using the gas volumetric technique described in Ref. 14, with, additionally, an accompanying buffer of ceramic $YBa_2Cu_3O_{6+x}$ placed in the sample preparation volume. For YBCO1, the oxygen content was deduced from Rietveld analysis of neutron data on the powder present in the furnace during the reduction and is estimated at $x=0.10(4)$. Both YBCO2 and Al-YBCO were measured on a four-circle diffractometer (to be described later). For YBCO2, we found an oxygen content $x=0.18(1)$ with a very good fit to the data [$R(F^2)=2\%$ and $\chi^2=1.9$], using SHELXL-93.[15] For the aluminum-doped sample, Al-YBCO, the oxygen content was found to be $x=0.25(4)$, with 14(3)% aluminum substituted on the Cu(1) site [$R(F^2)=3\%$].

The neutron scattering measurements were performed at Risø National Laboratory, on both a triple-axis spectrometer and a four-circle diffractometer. The first part of the measurement was made on the cold source triple-axis spectrometer TAS1 at a wavelength of 2.42 Å, using pyrolytic graphite filters to avoid higher-order contamination. The monochromator and the analyzer crystals were pyrolytic graphite, but some of the measurements were made without analyzer in order to relax the exit collimation.

The samples were wrapped in aluminum foil to avoid contamination by glue and were aligned with the (hhl) reflections in the scattering plane. Furthermore, the samples were sealed in an aluminum can filled with He gas to avoid reoxygenation above room temperature.

The measurements were performed between 2 and 450 K. The temperature range between 2 K and room temperature was handled in a standard ^{4}He cryostat. The range between room temperature and 450 K was performed in a small furnace specially designed for this purpose.

TAS1 was used to determine T_N on YBCO1, YBCO2 and Al-YBCO by following the $(\frac{1}{2},\frac{1}{2},2)$ reflection vs temperature, as well as the eventual existence of a T_2 by looking for a $(\frac{1}{2},\frac{1}{2},\frac{3}{2})$ reflection. A measurement of the $(h+\frac{1}{2},h+\frac{1}{2},l)$ magnetic Bragg peak intensities was also performed at 4.2 K for YBCO1 (see Table I).

The thermal source four-circle diffractometer TAS2 was used at a wavelength of $\lambda=1.047$ Å for two different purposes: first to accurately determine the oxygen contents for YBCO2 and Al-YBCO, and the amount of aluminum substituted on the Cu(1) site for this last sample (as described above) and, second, to measure at low temperature ($T=20$ K) magnetic structure factors for high values of the scattering vector **Q** on YBCO2. For this part a Displex closed-cycle refrigerator was used.

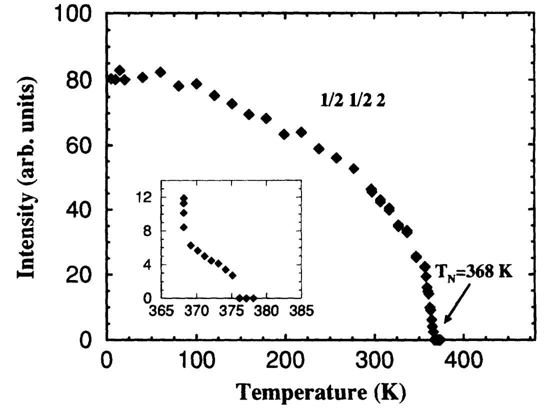

FIG. 1. Determination of T_N on $YBa_2Cu_3O_{6.18}$ (YBCO2) by following the magnetic Bragg peak $(\frac{1}{2},\frac{1}{2},2)$ vs temperature. The inset shows the critical scattering at the transition.

T_N was deduced from the onset of the magnetic Bragg reflection $(\frac{1}{2},\frac{1}{2},2)$. The critical scattering was estimated from the residual contribution above T_N (see inset in Fig. 1). The change in the intensity due to the temperature dependence of the Debye-Waller factor was estimated to be 2% between 2 and 420 K and therefore neglected.[16]

Finally, Néel temperatures T_N of 410(1), 368(1), and 411(1) K were deduced for YBCO1, YBCO2, and Al-YBCO, respectively (Figs. 1 and 2). For the 14% Al crystal, a $T_2=8(1)$ K was found (Fig. 2). This second magnetic transition, with a clear competing interaction of the two order parameters, demonstrates the high sample quality. It should be noted that the presence of 14% Al in the chains does not seem to affect T_N which could imply a scenario where the transition is driven by the *XY* anisotropy, which makes it quite insensitive to a modification of the magnetic coupling along the *c* axis.[17]

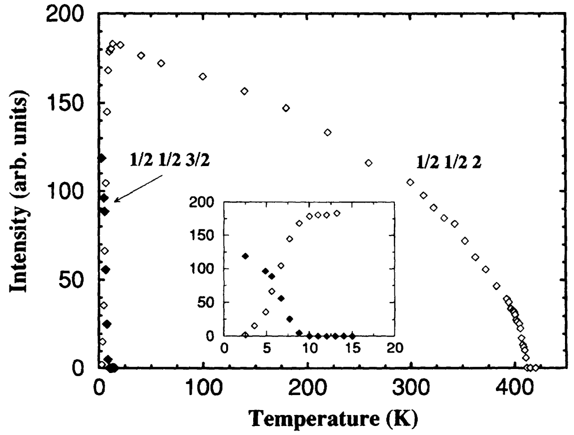

FIG. 2. Magnetic ordering in $YBa_2(Cu_{3-y}Al_y)O_{6.25}$ with $y=0.14$. Two transitions are observed at $T_N=411$ K and $T_2=8$ K by monitoring, respectively, the reflections $(\frac{1}{2},\frac{1}{2},2)$ (open diamonds) and $(\frac{1}{2},\frac{1}{2},\frac{3}{2})$ (solid diamonds) vs temperature.

This latter scenario could also be supported by our determination of the critical exponent β for the staggered magnetization. We determined β by fitting a power law $I \sim I_0(T_N - T)^{2\beta}$ to the region $0 < 1 - T/T_N \lesssim 10^{-1}$, and found $\beta = 0.26(2)$ for YBCO1, YBCO2, and Al-YBCO. The interpretation of the critical exponent β in $YBa_2Cu_3O_{6+x}$ is complicated by the existence of a strongly coupled bilayer. Indeed, only a lower limit of the magnetic coupling J_b inside the bilayer has been so far estimated at $J_b \geqslant 7 \times 10^{-2} J$, where J represents the antiferromagnetic (AF) superexchange interaction between Cu(2) sites in the CuO_2 plane.[2] Nevertheless, in the bilayered $K_3Mn_2F_7$ system, it has been found that the critical exponent is still very close to one of the single layer compound K_2MnF_4, both having a quasi-2D type of ordering.[18] Furthermore, since $YBa_2Cu_3O_{6+x}$ displays a weak XY anisotropy, our result should be compared to $\beta = 0.23$ obtained for the AF quasi-2D XY system $BaNi_2(PO_4)_2$,[19] or to $\beta = 0.22$ found for the ferromagnetic quasi-2D Heisenberg system K_2CuF_4, which also displays a weak XY type of perturbation.[20]

Next, we present the second part of the measurements concerning the magnetic structure factors. For the analysis of the magnetic structure factors measured on YBCO1 and YBCO2, we have used the following expression:[21]

$$|SF(\mathbf{Q})|^2 = 2\gamma^2(1+\cos^2\alpha) f^2(\mathbf{Q}) \mu^2 e^{-2W} \sin^2(\pi l z') \qquad (1)$$

where $SF(\mathbf{Q})$ is the magnetic structure factor, γ is equal to 0.269×10^{-12} cm, α is the angle between $\mathbf{Q}$ and its projection along the c axis, μ is the magnetic moment on the Cu(2) site, $f(\mathbf{Q})$ is the form factor, e^{-W} is the Debye-Waller factor and $z' = 1 - 2z$ [z being the coordinate of the Cu(2) with the origin taken on the Cu(1) site]. The coordinate z' is a sensitive parameter in Eq. (1), for which we used the value of 0.2786 determined from the four-circle measurement. A term $\frac{1}{2}(1+\cos^2\alpha)$ comes from the vectorial magnetic interaction with the assumption that the spins lie in the ab plane. For the form factor $f(\mathbf{Q})$ on the magnetic Cu(2) site, we used an *aspherical* expression[22] calculated for the $3d_{x^2-y^2}$ orbital.[2,23]

The validity of the model used [see Eq. (1)] is demonstrated in Table I and Fig. 3. To illustrate the deviation from a spherical magnetic form factor, we plot the form factor deduced from the experiment together with the spherical and aspherical expressions for a $3d_{x^2-y^2}$ unpaired electron in Fig. 3. From this analysis we deduced by least-squares fit a magnetic moment μ equal to $0.55(3)\mu_B$ and $0.44(3)\mu_B$ for YBCO1 and YBCO2, respectively. These values are in agreement with other published results,[2,3] and confirm the double effect of reduction (from the typical value $1.1\mu_B$ for a Cu^{2+} ion[24]), due to quantum spin fluctuations[25] and the covalency of the $3d_{x^2-y^2}$ orbital of the Cu(2) with neighboring oxygen $2p$ orbitals.[26]

In order to understand what drives the appearance of the second antiferromagnetic transition in $YBa_2(Cu_{3-y}Al_y)O_{6+x}$, we compare our results for pure and Al-doped $YBa_2Cu_3O_{6+x}$ to other results. Our first remark concerns the oxygen content x: YBCO1, YBCO2, and Al-YBCO correspond, respectively, to 0.1, 0.18, and 0.25. One could therefore wonder if such a transition does appear for a sufficient amount of oxygen. This is not supported by the result of Shamato *et al.*,[2] since they observed this second transition for $YBa_2Cu_3O_{6.15}$ with a $T_2 \sim 15$ K and a $T_N = 410$ K, where T_N confirms the low amount of oxygen in their sample.[27] Our second remark concerns the effect of the trivalent nonmagnetic aluminum impurities upon both the distribution and the amount of oxygen in the chains: both YBCO1 and Al-YBCO were reduced together in the same furnace, but they have quite different oxygen content (respectively, $x = 0.1$ and $x = 0.25$). This comes from the fact that the aluminum is trivalent and acts to keep a surrounding of oxygens in the basal plane, making a full reduction in oxygen most likely impossible, and preventing the formation of chains for a sufficient amount of aluminum. In fact, $YBa_2(Cu_{3-y}Al_y)O_{6+x}$ is tetragonal for any value of x, as soon as $y \geqslant 9\%$.[28]

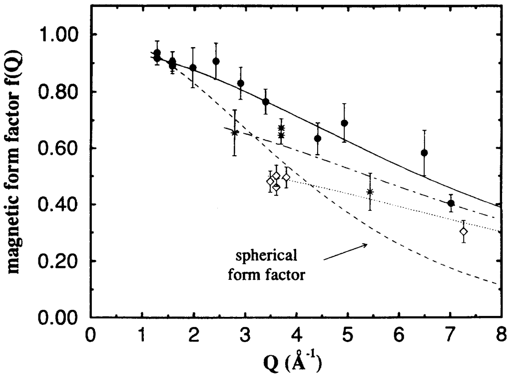

FIG. 3. Comparison between the form factors $f(\mathbf{Q})$ deduced from the experiment using Eq. (1) (symbols) and the calculated ones either for the spherical or aspherical unpaired $3d_{x^2-y^2}$ electron distribution (curves). The data were collected for YBCO1 on the triple-axis TAS1 and for YBCO2 on the four-circle TAS2. The different symbols ●, *, ◇ correspond to the $(\frac{1}{2},\frac{1}{2},l)$, $(\frac{1}{2},\frac{3}{2},l)$, and $(\frac{3}{2},\frac{3}{2},l)$ reflections, respectively. For the aspherical distribution, the solid curve corresponds to the $(\frac{1}{2},\frac{1}{2},l)$ reflections, the dot-dashed curve to the $(\frac{1}{2},\frac{3}{2},l)$ reflections, and the dotted curve to the $(\frac{3}{2},\frac{3}{2},l)$ reflections. The spherical form factor is given by the dashed curve.

The presence of aluminum impurities could cause a local segregation into regions, respectively, "rich" and "poor" in oxygen and favor the development of a localized moment on $Cu(1)^{2+}$ sites due to the bonding with a modified oxygen surrounding. Alternatively or in addition, preferential spin orientation could come from the deformation of $Cu(1)^{2+}$ orbitals bridging oxygen towards an Al impurity, which lowers the local symmetry of the crystalline electric field at the $Cu(1)^{2+}$ site. Further information concerning the clustering of Al impurities and their coordination(s) would be required for a deeper analysis. We note that in Refs. 1 and 2, which report a T_2 in "nominally" pure $YBa_2Cu_3O_{6+x}$, it is not clear whether the crystals had been contaminated by Al during the growth process. To close this discussion, we would like to mention that a systematic study of the effect on T_2 of both oxygen and aluminum contents is in progress, and that this second magnetic transition was also observed with 6% aluminum.[9]

Our major finding is the absence of the second antiferromagnetic transition in a high quality $YBa_2Cu_3O_{6+x}$ monocrystal without Al impurities. This basic result correlated with the observation of such a transition in a sample doped with 14% of aluminum allows us to conclude that this transition is strongly dependent on the magnetic coupling along the c axis. We suggest that results on the magnetism of $YBa_2Cu_3O_{6+x}$ and related compounds prepared in alumina crucibles (leading to aluminum contamination) should be interpreted accordingly.

We would like to thank P. A. Lingård and R. A. Hadfield for fruitful discussions. This work was partly supported under the E.E.C. "Human capital and mobility" program. P.S. was supported by the Natural Sciences and Engineering Research Council of Canada. E.B. is grateful for support by the "Deutsche Forschungsgemeinschaft."

---

[1] H. Kadowaki , M. Nishi, Y. Yamada, H. Takeya, H. Takei, S. M. Shapiro, and G. Shirane, Phys. Rev. B **37**, 7932 (1988).

[2] S. Shamato, M. Sato, J. M. Tranquada, B. J. Sternlieb, and G. Shirane, Phys. Rev. B **48**, 13 817 (1993).

[3] P. Burlet, C. Vettier, M. J. G. M. Jurgens, J. Y. Henry, J. Rossat-Mignod, H. Noel, M. Potel, P. Gougeon, and J. C. Levet, Physica C **153-155**, 1115 (1988).

[4] J. M. Tranquada, A. H. Moudden, A. I. Goldman, P. Zolliker, D. E. Cox, G. Shirane, S. K. Sinha, D. Vaknin, D. C. Johnston, M. S. Alvarez, A. J. Jacobson, J. T. Lewandowski, and J. M. Newsam, Phys. Rev. B **38**, 2477 (1988).

[5] J. Rossat-Mignod, L. P. Regnault, C. Vettier, P. Burlet, J. Y. Henry, and G. Lapertot, Physica B **169**, 58 (1991).

[6] P. Zolliker, D. E. Cox, J. M. Tranquada, and G. Shirane, Phys. Rev. B **38**, 6575 (1988); P. F. Miceli, J. M. Tarascon, P. Barboux, L. H. Greene, B. G. Bagley, G. W. Hull, M. Giroud, J. J. Rhyne, and D. A. Neumann, Phys. Rev. B **39**, 12 375 (1989).

[7] I. Mirebeau, C. Bellouard, M. Hennion, V. Caignaert, and E. Suard, J. Appl. Phys. **73**, 5689 (1993); J. L. Garcia-Munoz, J. Rodriguez-Carvajal, S. H. Kilcoyne, C. J. Boardman, and R. Cywinski, J. Magn. Magn. Mater. **104-107**, 555, (1992); I. S. Lyubutin, V. G. Terziev, S. V. Luchko, A. Ya. Shapiro, A. M. Balagurov, and G. A. Bonch-Osmolovskiy, Physica C **199**, 296 (1992).

[8] J. M. Tranquada, G. Shirane, B. Keimer, S. Shamato, and M. Sato, Phys. Rev. B **40**, 4503 (1989).

[9] E. Brecht (unpublished).

[10] There is a splitting of the energy levels of the $Cu^{2+}(3d^9)$ in the crystal field of its oxygen surrounding. The symmetry of this field leads to a $3d_{x^2-y^2}$ ground state.

[11] Ruixing Liang, P. Dosanjh, D. A. Bonn, D. J. Baar, J. F. Carolan, and W. N. Hardy, Physica C **195**, 51 (1992).

[12] W. N. Hardy, D. A. Bonn, D. C. Morgan, Ruixing Liang, and Kuan Zhang, Phys. Rev. Lett. **70**, 3999 (1993); C. C. Homes, T. Timusk, R. Liang, D. A. Bonn, and W. N. Hardy, Phys. Rev. Lett. **71**, 1645 (1993).

[13] Th. Wolf, W. Goldacker, B. Obst, G. Roth, and R. Flükiger, J. Cryst. Growth **96**, 1010 (1989).

[14] P. Schleger, W. N. Hardy, and B. X. Yang, Physica C **176**, 261 (1991).

[15] George M. Sheldrick, Acta. Cryst. **46**, 467 (1990).

[16] B. T. M. Willis and A. W. Pryor, *Thermal Vibrations in Crystallography* (Cambridge University Press, England, 1975).

[17] H. Casalta, H. Alloul, and J.-F. Marucco, Physica C **204**, 331 (1993).

[18] C. M. J. van Uijen, E. Frikkee, and H. W. de Wijn, Phys. Rev. B **19**, 509 (1979).

[19] L. P. Regnault, J. Y. Henry, J. Rossat-Mignod, and A. de Combarieu, J. Magn. Magn. Mater. **15-18**, 1021 (1980).

[20] Kinshiro Hirawaka and Hironobu Ikeda, J. Phys. Soc. Jpn. **35**, 1328 (1973).

[21] G. E. Bacon, *Neutron Diffraction* (Clarendon, Oxford, 1975).

[22] A. J. Freeman, Phys. Rev. **113**, 169 (1959).

[23] For the form factors $\langle j_0 \rangle$, $\langle j_2 \rangle$, and $\langle j_4 \rangle$, which appear in the expression for the anisotropic form factor $f(\mathbf{Q})$, we used the analytical approximations given in *International Tables for Crystallography*, edited by A. J. C. Wilson (Kluwer Academic, Dordrecht, 1992), Vol. C.

[24] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon, Oxford, 1970).

[25] E. Manousakis, Rev. Mod. Phys. **63**, 1 (1991).

[26] T. A. Kaplan, S. D. Mahanti, and Hyunju Chang, Phys. Rev. B **45**, 2565 (1992).

[27] In Ref. 1, Kadowaki *et al.* reported a second magnetic transition in $YBa_2Cu_3O_{6+x}$, with $x=0.35$ and $T_N=405$ K. This value of T_N is too high for such an oxygen content implying that either x was not determined properly or the sample had some contamination on the Cu(1) site leading to a shift of the charge transfer vs oxygen content.

[28] Thomas J. Kistenmacher, Phys. Rev. B **38**, 8862 (1988).