LOW TEMPERATURE X-RAY DIFFRACTION STUDIES ON $Tl_2Ba_2CaCu_2O_8$

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INTRODUCTION

The studied high-T_c superconductor is a member of the structural series $(TlO)_mBa_2Ca_{n-1}Cu_nO_{2+2n}$ with m=2 and n=2. The first refined structure data were published by Subramanian et al. [1], and evidence for superconductivity was first reported by Sheng and Hermann [2].The crystal structure is based on a body-centered tetragonal cell (space group I4/mmm, no.\ 139). The structure consists of alternating double layers of Cu-O and Tl-O, with Ca^{2+} cations between adjacent copper-oxygen sheets and Ba^{2+} cations between the copper-oxygen and thallium-oxygen layers. The oxygen atoms of the Tl-O layers are displaced from their symmetrical site and occupy split-atom sites with large temperature factors. There occurs also positional disorder on the cation sites, and evidence for stacking disorder and intergrowth with other members of this series has been reported [3].In recent neutron powder diffraction studies [4,5] no noticeable changes with temperature were observed in any structural parameters, so that the possible structural change was presumed to have only short range correlation. The pair-distribution function analysis showed a clear change in the local structure at the onset of superconductivity. In addition to the observed local displacements of Tl and O within the Tl-O sheets, correlated displacements of O and Cu perpendicular to the Cu-O plane were found. Furthermore, the arrangement of the O atoms appeared to be different above and below T_c. Anomalies in the temperature dependence of the Debye-Waller factor for Cu-O bonds near T_c have been observed for one member of the Tl-Ba-Ca-Cu-O series [6].

The aim of this study was to reveal the possible structural changes by measuring the variation of the unit cell dimensions when cooling the sample

below room temperature and below the transition temperature of superconductivity.

Experimental

The single crystal samples were prepared at the Institute of Crystallography, Academy of Sciences of the USSR, Moscow. The method of preparation is described earlier in [7]. The onset temperature of superconductivity for these samples is about 110 K. The crystal chosen for the measurement of the lattice parameters was irregularly shaped with minimum and maximum dimensions of about 0.05 mm and 0.12 mm. Measurements were performed using a Huber four-circle diffractometer equipped with a Displex closed-cycle two stage helium cryostat. The radiation used was graphite-monochromatized MoKα.

The sample was cooled stepwise from room temperature (298 K) down to 20 K. After each change of temperature, the position (height) of the crystal was checked and corrected, when necessary. The height adjustment was performed by equalizing the χ values of a reflection with low χ when centered at positive and negative 2θ values. The lattice parameter measurement at each temperature was performed by centering 40 reflections (as 20 Friedel pairs with opposite 2θ-values). The chosen 2θ-range of the reflections was such that the centering could be based on the $K\alpha_1$ line alone. The centering procedure at each temperature was started about half an hour later this temperature was reached. All measurements, except those at 225 K and 250 K, were performed during one cooling period, and the total time used for the experiment was about 72 hours. The stability of the measurement temperature was $\pm$ 0.5 K.

Results

The unit cell dimensions were refined with the program RAFIN [8], which relies on the basic equations developed by Busing and Levy [9], using all the four diffractometer setting angles. A preliminary analysis included the refinement of the systematic zero shifts of 2θ and χ in order to assure that the sample centering was not significantly changed during the cooling period. Symmetry constraints for the cell parameters were not applied in the first refinements, which showed that the deviations of the parameters from the values required by tetragonal symmetry were within the standard deviations of the values. The final results, given in Table 1, were obtained by a simultaneous least-squares refinement of the orientation matrix and the lattice parameters of a tetragonal cell. These results were also compared to the results obtained with the module

LATCON of the system of crystallographic programs XTAL [10] using 2θ-data only. The values of the parameter c calculated with the program LATCON were systematically smaller than the values obtained with the program RAFIN. This deviation is of the order of one standard deviation only, and it may be caused by a small error in the positioning of the sample crystal. The results for the parameter a did not differ from each other. The standard deviations obtained with the program LATCON were about one third of those obtained using the program RAFIN.

Table 1. The experimental values for the lattice parameters.

T(K)	a (Å)	c (Å)
298	3.8561(2)	29.366(3)
250	3.8540(3)	29.344(4)
225	3.8533(3)	29.333(4)
200	3.8525(2)	29.324(3)
190	3.8523(2)	29.320(4)
180	3.8521(3)	29.316(4)
160	3.8517(2)	29.310(3)
145	3.8513(3)	29.304(4)
135	3.8512(3)	29.300(5)
125	3.8509(2)	29.296(3)
115	3.8507(2)	29.294(4)
105	3.8506(3)	29.292(4)
95	3.8505(3)	29.290(4)
80	3.8503(2)	29.285(4)
60	3.8500(2)	29.281(4)
40	3.8498(3)	29.278(4)
20	3.8499(2)	29.277(3)

The ratios of the unit cell dimensions to the corresponding room temperature values, a/a_{298} and c/c_{298}, are presented graphically in figure 1. The parameter a decreases 0.16 % and the parameter c decreases 0.30 % when cooling from 298 K to 20 K. Each unit cell dimension as a function of temperature is represented by a fourth-order polynomial, the coefficients of which are determined by a least-squares fit of the experimental points. No significant improvement in fit could be achieved by adding higher-order terms. The obtained equations are $a = a_{298}[1 + k_{a1}\Delta T + k_{a2}(\Delta T)^2 + k_{a3}(\Delta T)^3 + k_{a4}(\Delta T)^4]$, where $k_{a1} = 1.39(3) \cdot 10^{-5}$ K^{-1}, $k_{a2} = 6.8(4) \cdot 10^{-8}$ K^{-2}, $k_{a3} = 2.6(2) \cdot 10^{-10}$ K^{-3}, $k_{a4} = 4.3(4) \cdot 10^{-13}$ K^{-4}, and $\Delta T = T - 298$ K; and a similar equation for c, with $k_{c1} = 1.72(4) \cdot 10^{-5}$ K^{-1}, $k_{c2} = 3.9(5) \cdot 10^{-8}$ K^{-2}, $k_{c3} = 1.7(2) \cdot 10^{-10}$ K^{-3}, and $k_{c4} = 3.9(4) \cdot 10^{-13}$ K^{-4}.

The linear expansion coefficients α_a and α_c for expansion along the directions a and c can be obtained by differentiating the lattice parameter

polynomials: $a_a = (1/a_{298})(da/dT)$. The calculated values for a_c at room temperature and at 110 K are $1.39 \cdot 10^{-5}\,K^{-1}$ and $0.44(3) \cdot 10^{-5}\,K^{-1}$, respectively, and the values for α_c at the same temperatures are $1.72(4) \cdot 10^{-5}\,K^{-1}$ and $0.99(4) \cdot 10^{-5}\,K^{-1}$. The ratio of α_c to α_a calculated from the values obtained from the third-order polynomials increases almost linearly from the value of 1.24 to 2.00 when the temperature is decreased by 100 K from the room temperature. Thereafter, when the temperature decreases by 100 K more the ratio increases very slowly to a value of 2.25, and the ratio is almost constant from 150 K down to 100 K. The numerically approximated derivative of the (α_c/α_a)-ratio has a local minimum at about 245 K and a local maximum at about 120 K, the latter value being just above the transition temperature of super-conductivity.

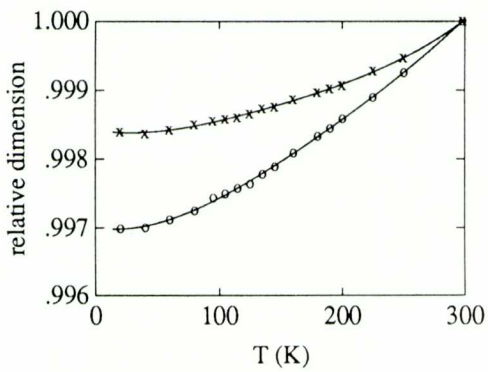

Figure 1. The relative unit cell dimensions $a(T)/a$(298K) and $c(T)/c$(298K). The experimental values are denoted by crosses (a) and circles (c).

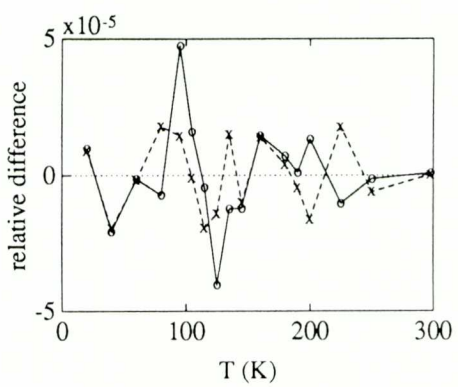

Figure 2. The relative differences, $(a_{exp} - a_{fit})/a_{exp}$ and $(c_{exp} - c\,f_{it})/c_{exp}$, between the experimental and calculated lattice parameters. The continuous lines (dashed for a, solid for c) are drawn only for clarity.

It can be seen from figure 1 that the lattice parameters decrease relatively smoothly with decreasing temperature, also through the superconducting transition point at T_c =110 K. The calculated polynomials seem to represent the experimental data quite satisfactorily. A closer examination of the results reveals that the difference between the experimental values of c and the values obtained from the polynomial is largest about 15 K above and 15 K below T_c (see figure 2). The maximum deviation is about twice the largest deviations elsewhere. A similar discrepancy is not found for the parameter a. By fitting two different polynomials to the measured values of c, one for the range 20 K - 110 K and another for the range 110 K - 298 K, the observed discrepancy near T_c decreases to the values obtained at other temperatures. It has to be emphasized, however, that the anomaly in the temperature dependence of the parameter c is very weak, the deviations being of the same order as the experimental errors. Consequently, any firm conclusions can hardly be drawn.

Intensity data collections for determining the structure and for relating the features observed in the behaviour of the lattice parameters as a function of temperature to the changes in the structure have been performed both below and above T_c (at 20 K, 60 K, 160 K and 298 K). The results of these measurements will be reported in a forthcoming paper [11]. The analysis of the room temperature data for the very same sample crystal is described also in [7].

ACKNOWLEDGEMENTS

Prof. V.I. Simonov and Dr. V.N. Molchanov from the Institute of Crystallography, Academy of Sciences of Russia, Moscow, are gratefully acknowledged for providing me with the single-crystal samples.

ABSTRACT

The unit cell dimensions of the superconductor $Tl_2Ba_2CaCu_2O_8$ were measured by single-crystal x-ray diffraction method over the temperature range 20 K - 298 K in an effort to observe the possible structural phase transitions. No clear evidence for a transition was found. At room temperature the values for the lattice parameters were a_{298} = 3.8561(2) Å and c_{298} = 29.366(3) Å, and the variation of the lattice parameters with temperature could be defined by the equation $a = a_{298}[1 + k_{a1}\Delta T + k_{a2}(\Delta T)^2 + k_{a3}(\Delta T)^3 + k_{a4}(\Delta T)^4]$, where k_{a1} = 1.39(3) · 10^{-5} K^{-1}, k_{a2} = 6.8(4) · 10^{-8} K^{-2}, k_{a3} = 2.6(2) · 10^{-10} K^{-3}, k_{a4} = 4.3(4) · 10^{-13} K^{-4}, and $\Delta T = T - 298$ K; and a similar equation for c, with k_{c1} = 1.72(4) · 10^{-5} K^{-1}, k_{c2} = 3.9(5) · 10^{-8} K^{-2}, k_{c3} = 1.7(2) · 10^{-10} K^{-3}, and k_{c4} = 3.9(4) · 10^{-13} K^{-4}. The parameter a decreased 0.16% and the parameter c decreased 0.30% when cooling the crystal from 298 K to 20 K. The temperature dependence of the parameter c showed a very small anomaly in the vicinity of the onset temperature for superconductivity.

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