

Superconducting Single Crystals of $Tl_2Ba_2CaCu_2O_8$ and $YBa_2Cu_4O_8$: Crystal Structures in the Vicinity of T_c

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Abstract

The structures of superconducting $Tl_2Ba_2CaCu_2O_8$ ($T_c \sim 110$ K) and $YBa_2Cu_4O_8$ ($T_c \sim 70$ K) were investigated by single-crystal X-ray diffraction techniques in a wide temperature range. Some of the structure parameters show anomalous behaviour in the vicinity of the critical temperature. The most pronounced structural change is the shift of the apical O atoms in CuO_5 pyramids towards the CuO_2 planes, indicating charge redistribution near T_c . This behaviour of the apical O atoms seems to be the common structural feature of hole-doped high- T_c superconductors. Another effect of charge redistribution at T_c concerns a very small decrease of in-plane Cu–O distances and/or O–O distances in CuO_5 pyramids. Both effects represent an averaged structure response to charge (hole) redistribu-

tion upon the phase transition to the superconducting state.

1. Introduction

The contribution of crystallography to the understanding of superconducting phenomena is very important. It should be noted that the most significant results were obtained by the groups of R. J. Cava (AT&T Bell Laboratories, USA), J. D. Jorgensen (Argonne National Laboratory, USA) and M. Marezio (Laboratoire de Cristallographie – CNRS, Grenoble, France). Many useful references may be easily found in the Superconductivity Papers Database (http://www.aist.go.jp/RIODB/sprcnd_etl/).

The crystal structure of high- T_c superconducting copper oxides has been studied in detail by X-ray and neutron diffraction techniques and high-resolution electron microscopy. Many structural aspects of these materials have been recently reviewed by Rao & Ganguli (1995), including various metal site substitutions, oxygen site vacancies, commensurate and incommensurate modulations. All copper oxide superconductors have a layered structure and show common crystal chemistry properties (Park & Snyder, 1995). This similarity has led to a general conception which directly links superconducting behaviour with the presence of CuO_2 planes while the other layers behave as charge-carrier reservoirs. Moreover, the concept of charge transfer between reservoir layers of the structure and two-dimensional CuO_2 planes which are responsible for the superconductivity was successfully used for evaluation of structure–property relations in different superconducting cuprates (Cava *et al.*, 1990; Jorgensen *et al.*, 1990; Marezio, 1991). The behaviour of the crystal structure during the phase transition to the superconducting state is one of the most important problems concerning superconductivity phenomena. Although some crystalline samples of high- T_c materials (mainly as powder) have already been investigated by neutron and X-ray diffraction techniques in a wide range of temperatures below and above T_c , the results by different authors are often in contradiction to each other. Nevertheless, the Cu–O distances and the

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possible anomalies in their behaviour are of considerable interest owing to their sensitivity to local charge distribution. The present paper reports the main results of a precision X-ray diffraction study of $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ ($T_c \sim 110$ K) and $\text{YBa}_2\text{Cu}_4\text{O}_8$ ($T_c \sim 70$ K) single crystals at several temperatures before the phase transition as well as at several temperatures in the superconducting state, thus allowing a more detailed analysis of the temperature dependence of the structure parameters. More detailed results for $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ and a brief preliminary communication about the results for $\text{YBa}_2\text{Cu}_4\text{O}_8$ were published earlier (Molchanov *et al.*, 1994, 1997).

Schematic presentation of the crystal structures of tetragonal $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ (space group $I4/mmm$) and orthorhombic $\text{YBa}_2\text{Cu}_4\text{O}_8$ (space group $Ammm$) is given in Fig. 1. 'Superconducting' perovskite-like slabs are similar in the two structures: two CuO_5 pyramid layers with Ca (or Y) cations between them and Ba cations located above and below them. In the case of $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$, the 'charge reservoir' slab involves two TlO layers packed according to the rock-salt motif, while, in $\text{YBa}_2\text{Cu}_4\text{O}_8$, this slab consists of double CuO chains running along the b axis. These two slabs, with different nature, are periodically alternating in both structures and the apical O atom in each CuO_5 pyramid serves as a bridge between the 'reservoir' part of the structure and the 'superconducting' CuO_2 planes. It is very probable that these apical O atoms should be more sensitive to changes in charge (hole) redistribution or changes in chemical bonding, if these really occur during the phase transition to the superconducting state. It should be noted that a second-order phase transition in

its pure form is not related to an atomic restructuring in a crystal. However, a change in the electronic structure of a compound should affect the nature of the chemical bonds in the crystal, so it should have a direct influence on the positional and thermal parameters of the crystal structure.

2. Structural models and lattice dynamics

As mentioned above, the majority of low-temperature investigations has been performed on powder samples. As there are only a few publications dealing with single-crystal diffraction studies, we find it quite useful to mention here some precepts we have followed in our low-temperature experiments. First, precise diffraction experiments have been carried out at room temperature using an Enraf-Nonius CAD-4F diffractometer (see *e.g.* Muradyan *et al.*, 1991). All equivalent reflections within one half of the reciprocal sphere were measured for a spherical sample of $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ ($\varnothing \sim 0.23$ mm), while for the plate-like crystal of $\text{YBa}_2\text{Cu}_4\text{O}_8$ ($0.21 \times 0.15 \times 0.03$ mm) the measurements were performed over the whole sphere of reciprocal space. In the latter case, it was important to optimize the crystal dimensions for proper absorption correction by using a reliability factor obtained by averaging the symmetry-equivalent reflections as a criterion for the best crystal shape description. The results of accurate refinements at room temperature were used in particular for producing the lists of most reliably measured reflections for each structure. These lists including several hundred reflections (approximately 15 independent reflections per refined parameter) were used for subsequent low-temperature measurements. Low-temperature diffraction measurements were performed on a Huber 5042 four-circle diffractometer equipped with a Displex 202 closed-cycle two-stage helium cryostat. Together with data collection, two-dimensional angular ω - 2θ scans for several reflections of type $h00$, $0k0$, $00l$, $hk0$, $k0l$ and $0kl$ were also performed at each temperature. These scans did not show any details that might be responsible for twinning and/or changes in mosaic spread upon cooling of crystals through the critical temperature. Owing to time limitation, only two octants of the reciprocal sphere were measured at low temperatures for $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ and only one for $\text{YBa}_2\text{Cu}_4\text{O}_8$. And finally, all refinements for each structure were based on the same independent reflections that were present in all temperature data sets.

In the following sections, several specific features of the crystal structures and refinements of $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ and $\text{YBa}_2\text{Cu}_4\text{O}_8$ single crystals are briefly discussed. On the one hand, this might give a sense of some structural aspects of cuprate superconductors. On the other hand, it gives a basic background for further explanation of possible changes in bond lengths in the vicinity of T_c .

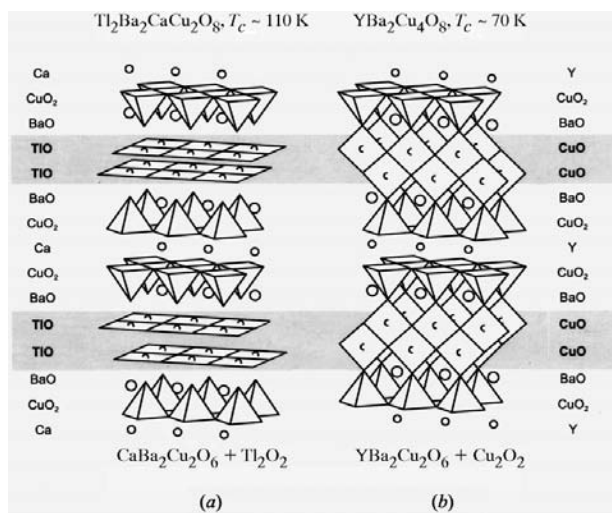


Fig. 1. Schematic presentation of the crystal structures of (a) $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ and (b) $\text{YBa}_2\text{Cu}_4\text{O}_8$. Grey areas indicate the difference in 'reservoir slab' constructions: (a) double Tl—O layers and (b) double CuO_4 chains inserted between planes of CuO_5 pyramids of 'superconducting slabs'. The chemical composition of layers is shown for both structures at the side of the figures.

2.1. $Tl_2Ba_2CaCu_2O_8$

A fragment of the tetragonal crystal structure of $Tl_2Ba_2CaCu_2O_8$ is presented in Fig. 2 on the left. Refinements were performed at five temperatures, *i.e.* at 296, 160, 130, 90 and 60 K. At the first, refinement of the site occupancies yielded a seeming excess of calcium and a deficit of thallium, indicating partial substitution of Tl by a lighter atom and Ca by a heavier atom. Isomorphous replacement of Ca by Tl proved to be the best model. This has been suggested in most other studies, although a full Ca site occupancy has also been reported (Ogborne *et al.*, 1992). According to previous structural studies, the Tl sites are partially either vacant (Morosin *et al.*, 1991) or isomorphously replaced by Ca (Subramanian *et al.*, 1988) or Cu atoms (Onoda, Kondoh, Fukuda & Sato, 1988). Based on crystal-chemistry reasons, Cu seems to be a better choice than Ca. However, placing Cu in the Tl site did not result in a significant lowering of the *R* factors, and the subsequent refinements of our structure model included the Tl site deficiency, without any additional atoms. According to the refined site occupancies, the chemical formula of the single crystal in question is $Tl_{1.85}Ba_2(Ca_{0.87}Tl_{0.13})Cu_2O_8$, with a possible occupation of Cu atoms in the main Tl-atom site. Calculation of average formal charge for

Cu atoms yields +2.16, which is comparable with +2.25 for stoichiometric $YBa_2Cu_4O_8$.

Further, refinement of the atomic displacement parameters for the Tl site at the fourfold axis leads to an unusually large anisotropy in the thermal motion of Tl as has also been observed in all previous studies. The thermal vibration ellipsoid is squeezed along the *c* axis while the ellipsoids of the other metal atoms are slightly elongated. The difference electron-density maps, constructed using the model with Tl at the fourfold axis, showed eight octagon-like poorly defined maxima, suggesting that the Tl atoms are displaced from its site to a general position. Refinement of this model gave clearly better results than the other ones with shifts of Tl atoms along the *a* axis or the *ab* diagonal. As a result, the total displacement of Tl atoms off the high-symmetry position is about 0.17 Å.

Sasaki *et al.* (1992) reported the existence of anharmonic thermal vibrations for Tl and Ba atoms in $Tl_2Ba_2CaCu_2O_8$ at room temperature. It is well known that anharmonic temperature factors and split positions are two alternative ways of structure evaluation. Usually, anharmonicity drops substantially upon cooling. However, we did not observe any essential changes in the Tl-atom shifts upon cooling the sample from room temperature down to 60 K. So, we believe that static disorder of the Tl (and O3) atoms is a more realistic model than a model with anharmonic thermal motion, although anharmonic effects may contribute to the structure to a certain extent.

Finally, according to the Fourier and difference Fourier maps of the O3 atom surroundings, there is no doubt that these atoms are highly disordered in the thallium–oxygen layers. Refinement with O3 at the fourfold axis leads to abnormally large and highly anisotropic thermal parameters. Introducing displacements from the ideal site along the *a* axis or *ab* diagonal leads to more normal values of the thermal parameters. Unfortunately, choosing the best displacement model is not possible based on the *R*-factor value, which is almost completely insensitive to the O3-atom shifts. However, especially in the case of simultaneous shifts along the *a* axis and *ab* diagonal (see Fig. 2), a visible depletion of the difference Fourier maps takes place around O3. It should be noted that introducing the O3 atom shifts has practically no effect on the values of the other refined parameters, and in the final refinements (in the study of the temperature dependence of the structure) O3 was kept at the site on the fourfold axis, as is shown in the upper part of Fig. 2. Typical values of reliability factors varied from 0.026 to 0.033 for final refinements at all temperatures.

The origin of the disorder in the Tl–O layers is a mismatch between the metrics of the CuO_2 layers, which control the lattice dimensions in the *ab* plane, and typical Tl^{3+} –O bond lengths in the rock-salt block of the structure. Dmowski *et al.* (1988) found strongly

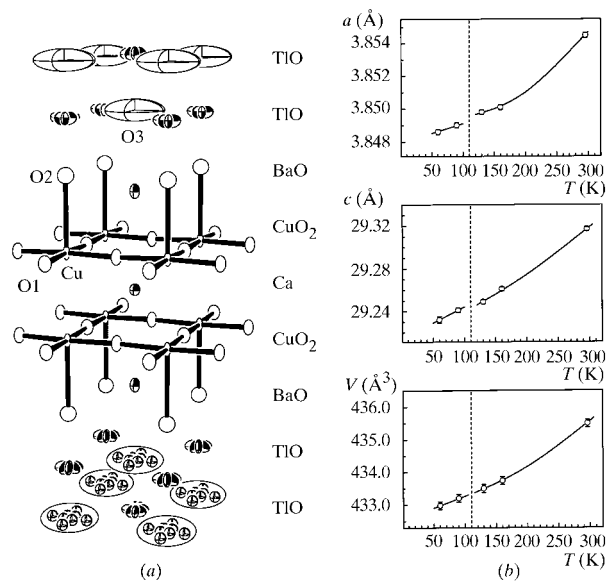


Fig. 2. A fragment of the crystal structure of $Tl_2Ba_2CaCu_2O_8$ (space group $I4/mmm$) (on the left). The numbering scheme and the Cu–O bonds are shown. The thermal ellipsoids are drawn as 95% surfaces. In the upper part of the figure, the O3 atoms in the double Tl–O layers are presented as large flattened ellipsoids. In the lower part, an alternative presentation of disordered O3 atoms enclosed in an ellipsoidal cavity is given. For clarity, the dimensions of isotropic spheres are twice reduced. The temperature dependence of the lattice constants and the cell volume are shown in the right part of the figure. The curves through the data are smooth spline fits to the points. Error bars are equal to one estimated standard deviation.

correlated local displacements of both Tl and O3 atoms from the high-symmetry sites using atomic pair-distribution analysis of pulsed-neutron scattering data. The reported displacements were 0.32 Å for Tl and 0.37 Å for O3, both shifts approximately along the ab diagonals. The O3-atom displacements obtained in our study agree well with these results but the Tl-atom displacement is about one half of the value reported. Moreover, Dmowski *et al.* (1988) found short-range ordering resulting from displacements of Tl and O3 in the Tl—O layer. The ordering leads to the formation of Tl—O chains or Tl₂O₂ clusters. The appearance of a weak modulation in Tl₂Ba₂CaCu₂O₈ (Moret *et al.*, 1990) may be the result of such local order in Tl—O layers.

The unit-cell dimensions of the tetragonal lattice were determined by a least-squares refinement of the setting angles of 18–20 well centred Friedel reflection pairs. Temperature variations of the unit-cell parameters and the lattice volume are shown in Fig. 2 on the right. The linear expansion coefficients, α ($\times 10^{-5} \text{ K}^{-1}$), for the lattice parameters and the unit-cell volume are $\alpha_a = 0.7(1)$, $\alpha_c = 1.2(1)$, $\alpha_v = 2.4(2)$ in the temperature range 60–296 K. The temperature dependence of the unit-cell volume did not show any discontinuities, which agrees with a second-order phase transition. A more detailed analysis of the temperature dependence of the lattice parameters for another crystal of the same compound (Blomberg, 1992) did not reveal any significant discontinuities, either. However, these results indicated a small anomaly in the length of the c axis near T_c . The effect was of the same type as the one observed by Srinivasan *et al.* (1988) for YBa₂Cu₃O₇, where the lattice parameter c was observed to increase abruptly at T_c , recovering its original value as the temperature was reduced below T_c . Possibly, a small anomaly in the length of the a axis of tetragonal Tl₂Ba₂CaCu₂O₈ also takes place, indicating the tendency to a small sudden shrinkage of the structure in the ab plane at a temperature just below T_c . However, both lattice effects are too tiny to be identified as a discontinuous change, and more experimental points would have been required in the close vicinity of T_c .

2.2. YBa₂Cu₄O₈

A fragment of the orthorhombic crystal structure of YBa₂Cu₄O₈ ($T_c \sim 70 \text{ K}$) is presented in Fig. 3 on the left. Refinements were carried out for four different temperatures above T_c , *i.e.* at 295, 95, 89 and 77 K, as well as at four different temperatures in the superconducting state, *i.e.* at 65, 59, 53 and 20 K. It should be noted that, in contrast with Tl-containing cuprates, YBa₂Cu₄O₈ is free from mixed-ion effects and relatively free from lattice defects. Nevertheless, various structural defects in YBa₂Cu₄O₈ have been observed by high-resolution electron microscopy (Hashimoto *et al.*, 1996), which include triple Cu—O chains resulting from the

insertion of one extra Cu—O chain at the location of the original double Cu—O chains, planar faults consisting of thin 90° rotation twins about the c axis and the co-existence of YBa₂Cu₄O₈ blocks and YBa₂Cu₃O₇ layers within one crystal. These defects, if they are occasionally distributed in the crystal and if their amount is not negligible, contribute to the diffraction of the main phase and lead to the appearance of additional peaks in the Fourier and difference electron density maps (see Schwer *et al.*, 1995). Refinements of the crystal structure of YBa₂Cu₄O₈ at room temperature, including anisotropic extinction parameters as well as anharmonic temperature parameters of Y, Ba and Cu atoms up to fourth order, yield a very low value of the R factor, less than 0.009, for the final averaged reflection array, thus attesting to the high quality of the diffraction data. However, we failed in the adequate interpretation of deformation electron-density maps because of the existence of weak additional peaks located around all heavy atoms along the c axis. Details of these results will be published elsewhere.

Refinements of the crystal structure of YBa₂Cu₄O₈ at low temperatures were performed with isotropic extinction parameters and anisotropic thermal param-

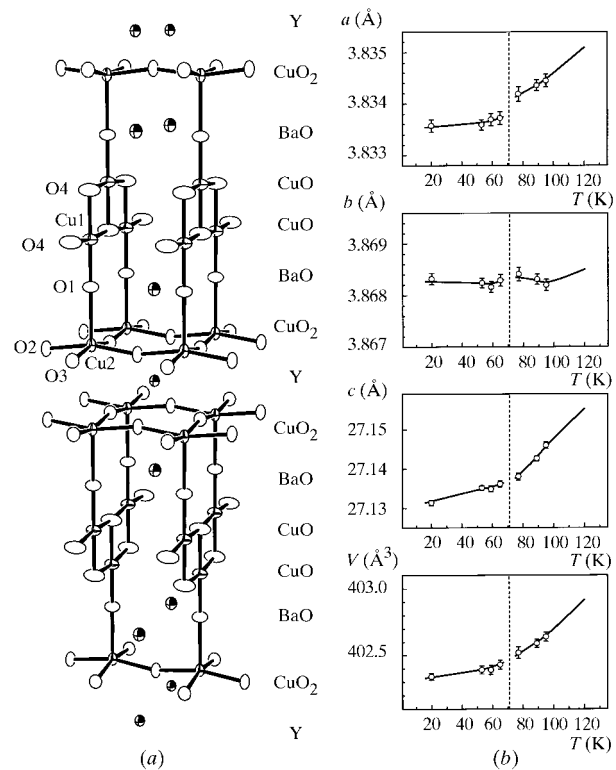


Fig. 3. A fragment of the crystal structure of YBa₂Cu₄O₈ (space group $Ammm$) (left). The numbering scheme and the Cu—O bonds are shown. The thermal ellipsoids are drawn as 95% surfaces. The temperature dependence of the lattice constants and the cell volume are shown in the right part of the figure. The curves through the data are smooth spline fits to the points.

eters for all atoms. While examining site occupancies, no significant deviation from stoichiometry was found. No additional interstitial sites were found either. The compound is therefore found to be stoichiometric, $\text{YBa}_2\text{Cu}_4\text{O}_8$. However, the reduced value of $T_c \sim 70$ K of our sample, in comparison with the highest achieved $T_c = 80$ K, suggests a small amount of Al incorporated into the crystal, which is usual for samples grown in an Al_2O_3 crucible (see *e.g.* Dabrowski *et al.*, 1992). Typical values of reliability factors varied from 0.011 to 0.019 for final refinements at all temperatures, thus attesting to the high quality of the results obtained.

Temperature variations of the unit-cell parameters and the lattice volume are shown in Fig. 3 on the right. The linear expansion coefficients, α ($\times 10^{-5} \text{ K}^{-1}$), for the lattice parameters and the unit-cell volume are $\alpha_a = 0.67$ (4), $\alpha_b = 0.32$ (4), $\alpha_c = 1.20$ (3), $\alpha_V = 2.2$ (1) within the temperature range 20–296 K. Note that values of α_a , α_c and α_V are very close to those for $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$, while α_b is approximately two times less than α_a , thus reflecting the rigidity of the structure along double Cu–O chains. The unit-cell dimensions were determined by a least-squares refinement of the setting angles of 28 well centred high-angle reflections measured in both the positive and negative 2θ region. The same reflection set was used to control careful centring of the crystal at each temperature. Deviations of the crystal from the centre of the goniometer did not exceed 0.035 mm, and were used for minor correction of setting angles before unit-cell refinement. As a result, the precision in measuring the cell parameters (5.5×10^{-5}) was higher than that of an X-ray powder study [1.0×10^{-4} (Alexandrov *et al.*, 1990)] but still lower than that of the neutron powder diffraction data [2.5×10^{-5} (Kaldis *et al.*, 1989)]. In contrast to previous studies, the a axis appears to have a small abrupt decrease at a temperature just below T_c . A very small smooth maximum might be present along the b axis around T_c , but the lack of accuracy prevents any certain conclusion. Nevertheless, these effects are consistent with the observation of small positive jumps in expansivity along the a and b axes exactly near T_c and negative expansivity of the b axis below 60 K (Meingast *et al.*, 1993). Also, these facts demonstrate that superconductivity in $\text{YBa}_2\text{Cu}_4\text{O}_8$ favours a lattice with a larger orthorhombic distortion. Orthorhombicity, $2000(b-a)/(b+a)$, increases from 8.1 (1) at room temperature to 9.0 (1) at 20 K. The c -axis values show clear inflection near T_c , while the cell volume expands normally with temperature and the data can be fitted with a smooth curve over the entire temperature range. The latter agrees with a second-order phase transition.

3. Temperature dependence of the average structure

As mentioned above, the cuprate superconductors often contain various defects. The situation when some

of the crystallographic site are occupied by different species of atoms or are partially vacant is most common [*e.g.* $\text{Tl}_{1.85}\text{Ba}_2(\text{Ca}_{0.87}\text{Tl}_{0.13})\text{Cu}_2\text{O}_8$ in this work]. Extended defects such as stacking faults, dislocations and intergrowths are readily investigated by electron microscopy [see Hashimoto *et al.* (1996) for $\text{YBa}_2\text{Cu}_4\text{O}_8$]. Besides, local structure techniques, such as atomic pair-distribution analysis of pulsed-neutron scattering data or ion channelling, were also used for the structure characterization of superconducting materials in a wide range of temperatures. In the former method, the pair-distribution function is interpreted in terms of the probability of finding two atoms separated by a particular distance and gives information about the local correlation of atomic displacements. The latter technique is very sensitive to a small displacement (~ 0.01 Å) of atoms from their regular lattice sites, however, it cannot distinguish between static and dynamic displacement. Toby *et al.* (1990) determined by atomic pair-distribution analysis that in addition to the previously observed local displacements of Tl and O3 atoms within the Tl–O sheets in $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$, correlated displacements of O1 and Cu atoms in the direction perpendicular to the Cu–O plane also exist and that the arrangement of the O1 atoms appears to be quite different above and below T_c . The local structure of superconducting $\text{YBa}_2\text{Cu}_4\text{O}_8$ was studied by atomic pair-distribution analysis at temperatures ranging from 10 to 250 K by Sendyka *et al.* (1995). According to their brief communication, collective displacements of chain O atoms forming polarized microdomains of size less than 20 Å were found to be dynamic. It was also found that the chain oxygen O4 and the apical oxygen O1 atoms are displaced from the average crystallographic sites by about 0.1 and 0.05 Å, respectively. In addition, displacements of in-plane O2 and O3 atoms in the direction parallel to the c axis by about 0.03 Å were also observed.

The ion-channelling technique was used to investigate atomic displacement related to static or dynamic distortion in $\text{YBa}_2\text{Cu}_3\text{O}_7$ by Sharma *et al.* (1996). It was found that the displacement amplitude of Cu atoms drops by about 0.01–0.015 Å in the ab plane when the temperature is lowered across $T_c = 92.5$ K, which means that the structure changes to a more ordered state with transition to the superconducting state. Below T_c , no measurable change was observed and the structure keeps its highly ordered state. In contrast with ion-channelling results, neutron powder diffraction data for $\text{YBa}_2\text{Cu}_3\text{O}_7$ have shown no evidence for an anomaly in any structure parameter in the vicinity of T_c (Sharma *et al.*, 1991). The fact of seeing the anomalous displacements at T_c by only the ion-channelling technique indicates that these displacements are either dynamic in character or static in such a way that fails to preserve the overall crystal symmetry and so are invisible in a neutron diffraction study.

Before a description of the possible structural changes in the vicinity of T_c , it must be emphasized that all our results concern the averaged structure. Correlated or uncorrelated local shifts or movements, as well as partial ordering of atoms in the mixed sites, which were not taken into account in our structural model, may still be accumulated in the refined parameters (*e.g.* as enlarged atomic displacement parameters). Changes in the local atomic arrangements near T_c [as detected by Toby *et al.* (1990) for $Tl_2Ba_2CaCu_2O_8$ or by Sendyka *et al.* (1995) for $YBa_2Cu_4O_8$] would affect the centre-of-mass positions and could, in principle, be seen in the average structure model as small changes in the atomic positions and thermal parameters.

3.1. $Tl_2Ba_2CaCu_2O_8$

The variation of selected interatomic distances for the $Tl_2Ba_2CaCu_2O_8$ structure is shown in Fig. 4. The scheme on the left upper side of the figure represents the junction of the CuO_5 pyramid with Tl and O atoms in the Tl—O layer and shows the most significant shifts of O atoms in the close vicinity of T_c . The in-plane distance Cu—O1 shows a clear shortening during the transition to the superconducting state. Since the CuO_2 plane is almost flat and the deviation of the Cu atom off the pyramid base stays approximately constant during the temperature lowering, the temperature dependence of

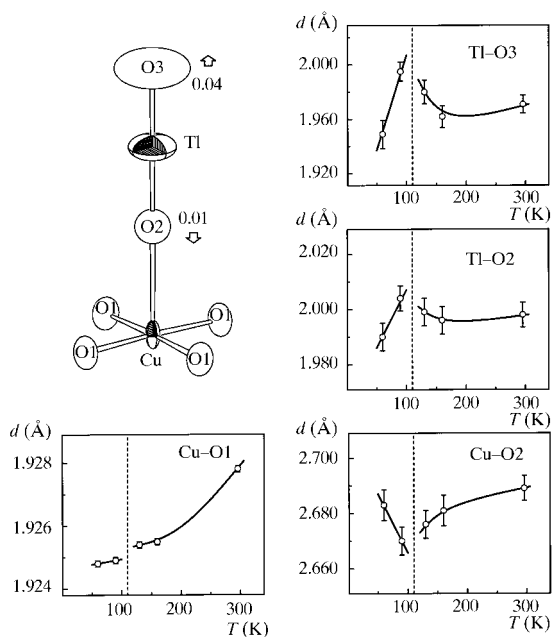


Fig. 4. Temperature dependence of selected interatomic distances for the $Tl_2Ba_2CaCu_2O_8$ structure. Curves are guides for the eye, just stressing the trends of variation. The scheme in the left upper part of the figure represents the junction of the CuO_5 pyramid with the Tl and O atoms in the Tl—O layer. For clarity, both the Tl and O atoms are presented as flattened ellipsoids. Grey arrows show the most significant shifts of O atoms in the close vicinity of $T_c \sim 110$ K.

the interatomic distance Cu—O1 is practically the same as that of the lattice parameter a . The distance from the Cu atom to the apical oxygen O2 atom has a minimum near the critical temperature, and below T_c it is abruptly increased. This behaviour might be related to that of the vibration frequency of the O2 atom, which hardens as temperature is lowered to T_c and then at T_c begins to soften (Chrzanowski *et al.*, 1991). The Tl—O2 and Tl—O3 distances show a clear tendency for a maximum near T_c . While the former distance is related to the distance Cu—O2, thus reflecting changes in this distance, the latter reflects a decrease in the buckling of the Tl—O layers around T_c . It should be noted that buckling of the CuO_2 plane also slightly decreases just below T_c . In conclusion, in the vicinity of T_c , the oxygen pyramid of copper is slightly compressed along the c axis and shows very tiny compression in the ab plane at temperatures just below T_c .

3.2. $YBa_2Cu_4O_8$

The variation of selected interatomic distances for the $YBa_2Cu_4O_8$ structure is shown in Fig. 5. The scheme on the left upper side of the figure represents the junction of the CuO_5 pyramid with the CuO_4 square of double Cu—O chains and shows the most significant shifts of O atoms in the close vicinity of T_c . According to this

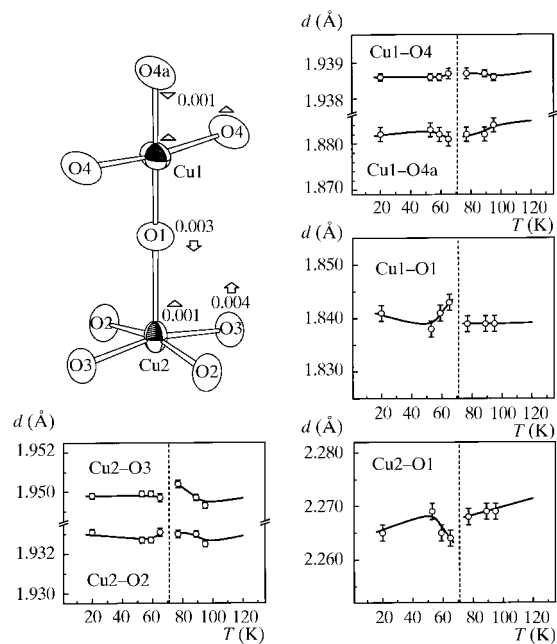


Fig. 5. Temperature dependence of selected interatomic distances for the $YBa_2Cu_4O_8$ structure. Curves are guides for the eye, just stressing the trends of variation. The scheme in the left upper part of the figure represents the junction of the CuO_5 pyramid with the CuO_4 square of double Cu—O chains. Grey arrows show the most significant shifts of Cu and O atoms in the close vicinity of $T_c \sim 70$ K.

scheme, it is clearly seen that the bridging O1 atom moves towards the CuO₂ plane at temperatures just below T_c . The corresponding contraction of the Cu2—O1 bond has already been observed for YBa₂Cu₄O₈ by neutron powder diffraction (Izumi, 1991). In our work, the shortening of the Cu2—O1 distance is more pronounced (0.005 Å) and sharp in the temperature range $T_c \pm 20$ K. Elongation of the Cu1—O1 distance just mirrors this effect. Although the O2 and O3 atoms are almost similar in bonding with the Cu2 atoms, their behaviour across T_c is different. While the position of the O2 atom shows a slight minimum in the vicinity of T_c , which leads to a corresponding smooth maximum in the Cu—O2 distance, the O3 atom abruptly moves up, decreasing the Cu—O3 distance, and thus making the Cu—O distances in the CuO₂ plane more equivalent just below T_c . Finally, the position of the O4 atom stays almost constant from room temperature to 20 K. It should be noted that the reservoir slab with double CuO chains (and short Cu—O4 bonds) is less compressible upon cooling. Temperature variation of both Cu positions is much less significant (in Å) and follows the same pattern as for the O4 atom: a smooth maximum along the c axis. In addition, as the temperature is lowered through T_c , the Ba atom seems to have a small jump-like shift in the direction of the double CuO chain, stressing the corresponding contraction of the Ba—O1 distance.

In other words, the most significant changes in the interatomic distances involve O atoms in the CuO₅ pyramid. First, the O1 and Cu2 atoms move toward each other. As a result, the Cu2—O1 distance shows a minimum just below (or at) T_c . Further, the displacement of the O1 atom is accompanied by the synchronous shift of the O2 atom in the way that the O1—O2 distance remains nearly constant in the range 20–100 K. In contrast to this ‘rigid’ pyramid edge, the longer O1—O3 distance shows a sudden decrease at $T < T_c$ owing to the movement of the O3 atoms along the c axis. In conclusion, in the vicinity of T_c , the oxygen pyramid of copper is slightly compressed along the c axis and shows a very tiny compression in the ab plane at temperatures just below T_c .

4. Structure response to superconductivity

Further comparison of our data with the results obtained from other high- T_c materials reveals one structural feature that seems to be common for those high- T_c crystals which contain CuO₅ pyramids with short in-plane Cu—O bonds and a longer bond to the apical O atom. Note that the presence of apical O atoms is necessary for hole-doping in the CuO₂ sheets. Cuprates having CuO₂ sheets with no apical O atoms have not been doped with holes until now. Figs. 6(a) and (b) represent very similar temperature dependencies of the apical Cu—O bonds in the single crystals of three

structures, namely YBa₂Cu₄O₈, Tl₂Ba₂CaCu₂O₈ and Tl₂Ba₂Ca₂Cu₃O₁₀. In all the cases, the Cu—O bond has a minimal value in the close vicinity of T_c , thus reflecting a charge redistribution between the ‘reservoir layer’ and the ‘superconducting slab’ *via* the bridging O atoms. It should be noted that longer Cu—O apical bonds, such as in the Tl-based superconductors, decrease more readily than shorter bonds in yttrium compounds. It is worth mentioning that powder diffraction results do not always clearly show the effect of the Cu—O bond shortening. For example, a precise neutron powder diffraction study of YBa₂Cu₄O₈ (Kaldis *et al.*, 1989) has shown no evidence for an anomaly in any structural parameter in the vicinity of T_c . This conclusion was later confirmed by an X-ray powder diffraction study (Alexandrov *et al.*, 1990). On the other hand, a neutron powder investigation of another sample has revealed the contraction of the Cu—O(apical) bond, possibly with a very smooth minimum near T_c (Izumi, 1991). Also, in the ceramic sample of Ca-doped (Y_{0.9}Ca_{0.1})Ba₂Cu₄O₈, studied by high-resolution time-of-flight neutron diffraction (Trounov *et al.*, 1994), the effect of shortening of the Cu2—O1 distance was even more pronounced

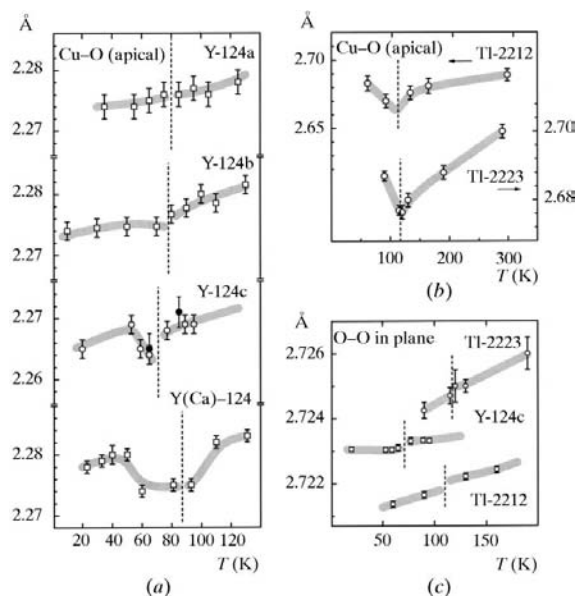


Fig. 6. (a) Temperature variation of the Cu—O(apical) distances in the CuO₅ pyramid in the YBa₂Cu₄O₈ structure: Y-124a neutron powder data (Kaldis *et al.*, 1989); Y-124b neutron powder data (Izumi, 1991), Y-124c our data for single-crystal plus two points (solid circles) for single-crystal study from Bordet *et al.* (1989); Y(Ca)-124 neutron powder data for (Y_{0.9}Ca_{0.1})Ba₂Cu₄O₈ (Trounov *et al.*, 1994). All variations are plotted on the same scale. Powder diffraction data are presented as squares, single-crystal data as circles. Bold grey curves are guides for the eye, just stressing the trends of variation. Dashed vertical lines represent T_c . All notations are valid for (a) and (b). (b) Temperature variation of the Cu—O(apical) distances in the CuO₅ pyramid in Tl₂Ba₂CaCu₂O₈ (Tl-2212; Molchanov *et al.*, 1994) and Tl₂Ba₂Ca₂Cu₃O₁₀ (Tl-2223; Hasegawa *et al.*, 1996) structures. (c) Temperature variation of O—O in-plane distances for Y-124c, Tl-2212 and Tl-2223.

(~ 0.01 Å) than for the single crystal of $\text{YBa}_2\text{Cu}_4\text{O}_8$. Possibly the inconsistency of the results depends first on the crystalline sample quality and then also on sample volume, which is usually larger for powder diffraction techniques.

Another effect of charge redistribution at T_c concerns a very small decrease of in-plane Cu—O distances (Molchanov *et al.*, 1994) and/or O—O distances in the CuO_5 pyramid (Hasegawa *et al.*, 1996). Fig. 6(c) represents the temperature variations of the O—O in-plane distance in single crystals of three different structures. In all the cases, the O—O in-plane distances show a small but detectable jump-like decrease at T_c . Together with the shortening of the Cu—O(apical) bond near T_c , this leads to a closer oxygen environment around the Cu atoms in the CuO_5 pyramid, thus reflecting an increase in the positive charge in the CuO_2 planes. The bond valence sum calculation reflects an additional increase (~ 0.004) of formal positive charge of the Cu atoms in the CuO_2 planes to an initial value of 2.12 for $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ and 2.17 for $\text{YBa}_2\text{Cu}_4\text{O}_8$ exactly at T_c .

As mentioned above, a change in the electronic structure of a compound should have a direct influence on the atomic displacement parameters of the crystal structure. In the case of superconducting materials, the situation is complicated because of the local correlation of dynamic displacements of atoms at low temperatures. These local displacements as well as changes in their character near T_c should contribute to refined values of thermal parameters of atoms in the structure.

Fig. 7(a) represents temperature variations of root-mean-square displacements, u (Å), for the in-plane O1 atom in the structure of $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$. The smallest amplitude of the thermal vibration of the O1 atom, u_a , is naturally directed along the short Cu—O1—Cu bonds. The amplitude u_b , of intermediate magnitude, is

perpendicular to these bonds, lies in the cuprate plane and corresponds to rotation of the CuO_5 pyramid around the c axis. The largest amplitude, u_c , is perpendicular to the cuprate plane. All these parameters exhibit anomalous behaviour near T_c . While amplitudes u_a and u_b show minimal values at T_c , thus indicating some strengthening of the Cu—O bonds, the amplitude u_c drops abruptly (~ 0.02 Å) when the temperature is lowered from 130 to 90 K. The latter observation is, at least qualitatively, in agreement with the results of Toby *et al.* (1990) who reported correlated Cu- and O1-atom displacements perpendicular to the cuprate plane, the difference in the maximal value of the O-atom displacements above and below T_c being ~ 0.05 Å.

In the structure of $\text{YBa}_2\text{Cu}_4\text{O}_8$, the in-plane O2 and O3 atoms are almost similar in bonding with the Cu2 atoms. For clarity, their displacement amplitudes along the Cu—O bonds (u_a), perpendicular to these bonds (u_b) and perpendicular to the CuO_2 plane (u_c) are averaged and presented in Fig. 7(b) in the same manner as in Fig. 7(a). The amplitude u_a shows a minimal value just below T_c , indicating some strengthening of the Cu—O bonds in the CuO_2 plane, while a small maximum of u_b at the same temperatures corresponds to an increase of the rotational instability of the CuO_5 pyramid. The decrease in the u_c is less prominent in comparison with that of the O1 atom in Fig. 7(a), possibly due to a more pronounced buckling of the CuO_2 planes in the $\text{YBa}_2\text{Cu}_4\text{O}_8$ in comparison with the $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ where these planes are almost flat. Nevertheless, the anomalous behaviour of u_a and u_c displacement amplitudes seems to be quite similar for both structures, confirming some hardening of O-atom movements near T_c .

5. Concluding remarks

Detailed comparison of our precision X-ray diffraction studies of $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ and $\text{YBa}_2\text{Cu}_4\text{O}_8$ single crystals with some published results on other high- T_c superconducting samples provides the following insights into the averaged structure response to charge (hole) redistribution upon the phase transition to the superconducting state.

The most significant changes in the interatomic distances involve O atoms in the CuO_5 pyramid. The Cu—O(apical) distance is minimal exactly in the vicinity of T_c . This effect is accompanied by a small jump-like decrease of Cu—O and/or O—O distances in the CuO_2 plane. Both effects clearly indicate an increase of formal positive charge on the Cu atom, thus reflecting a transfer of a small portion of holes from the reservoir layer to the CuO_2 planes. It seems to be the common structural feature for hole-doped high- T_c superconductors.

Anomalous changes of atomic displacement parameters of in-plane O atoms could be interpreted in terms of the strengthening of Cu—O bonds, decreasing or

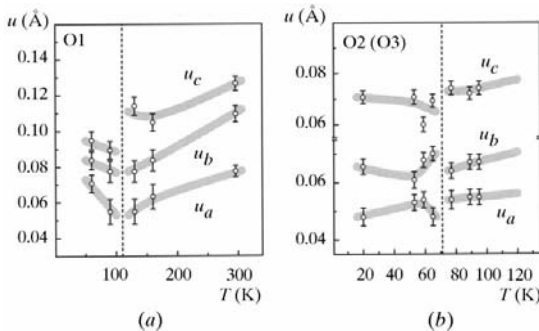


Fig. 7. (a) Temperature variation of the root-mean square displacements, u (Å), of the in-plane O1 atom in the $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ structure; u_a corresponds to displacement along the Cu—O—Cu bonds, u_b to displacement perpendicular to these bonds and u_c to displacement perpendicular to the CuO_2 planes. (b) Temperature variation of the root-mean-square displacements, u (Å), of in-plane O2 and O3 atoms in the $\text{YBa}_2\text{Cu}_4\text{O}_8$ structure. Displacements identical in character are averaged for these two atoms, notation being the same as in (a).

increasing of rotational instability of CuO_5 pyramids and hardening of thermal vibration along the c axis. Also, these effects must be closely related to the changes in the character of locally correlated dynamic displacements of atoms above and below T_c . According to local probe techniques, such as ion channelling and atomic pair-distribution analysis, changes in the buckling of CuO_2 planes and other cooperative movements of Cu and O atoms are always much more pronounced than those evaluated by single-crystal or powder diffraction techniques.

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References

- Alexandrov, O. V., François, M., Graf, T. & Yvon, K. (1990). *Physica (Utrecht)*, **C170**, 56–58.
- Blomberg, M. K. (1992). *Bull. Soc. Catalanes Fís. Quím. Mater. Technol.* **13**, 173–178.
- Bordet, P., Hodeau, J. L., Argoud, R., Miller, J., Marezio, M., Martinez, J. C., Prejean, J. J., Karpinski, J., Kaldis, E., Rusiecki, S. & Bucher, B. (1989). *Physica (Utrecht)*, **C162–164**, 524–525.
- Cava, R. J., Hewat, A. W., Hewat, E. A., Batlogg, B., Marezio, M., Rabe, K. M., Krajewski, J. J., Peck, W. F. & Rupp, L. W. (1990). *Physica (Utrecht)*, **C165**, 419–433.
- Chrzanowski, J., Fortier, N., Cragg, A., Burany, S., Heinrich, B. & Irwin, J. C. (1991). *Physica (Utrecht)*, **C185–189**, 649–650.
- Dabrowski, B., Zhang, K., Pluth, J. J., Wagner, J. L. & Hinks, D. G. (1992). *Physica (Utrecht)*, **C202**, 271–276.
- Dmowski, W., Toby, B. H., Egami, T., Subramanian, M. A., Gopalakrishnan, J. & Sleight, A. W. (1988). *Phys. Rev. Lett.* **28**, 2608–2611.
- Hasegawa, M., Matsushita, Y. & Takei, H. (1996). *Physica (Utrecht)*, **C267**, 31–34.
- Hashimoto, K., Akiyoshi, M., Wishniewski, A., Jenkins, M. L., Toda, Y. & Yano, T. (1996). *Physica (Utrecht)*, **C269**, 139–148.
- Izumi, F. (1991). *Physica (Utrecht)*, **C190**, 35–38.
- Jorgensen, J. D., Veal, B. W., Paulicas, A. P., Novicki, L. J., Crabtree, L. J., Claus, H. & Kwok, W. K. (1990). *Phys. Rev. B*, **41**, 1863–1877.
- Kaldis, E., Fisher, P., Hewat, A. W., Hewat, E. A., Karpinski, J. & Rusiecki, S. (1989). *Physica (Utrecht)*, **C159**, 668–680.
- Marezio, M. (1991). *Acta Cryst.* **A47**, 640–654.
- Meingast, C., Karpinski, J., Jilek, E. & Kaldis, E. (1993). *Physica (Utrecht)*, **C209**, 591–596.
- Molchanov, V. N., Simonov, V. I., Blomberg, M. K. & Merisalo, M. J. (1997). *JETP Lett.* **66**, 534–539.
- Molchanov, V. N., Tamazyan, R. A., Simonov, V. I., Blomberg, M. K., Merisalo, M. J. & Mironov, V. S. (1994). *Physica (Utrecht)*, **C229**, 331–345.
- Moret, R., Gougeon, P., Potel, M., Levet, J.-C. & Noel, H. (1990). *Physica (Utrecht)*, **C168**, 315–321.
- Morosin, B., Ginley, D. S., Venturini, E. H., Baughman, R. J. & Tigges, C. P. (1991). *Physica (Utrecht)*, **C172**, 413–422.
- Muradyan, L. A., Molchanov, V. N., Tamazyan, R. A., Simonov, V. I., Shibaeva, R. P., Korotkov, V. E., Kolesnikov, N. N. & Kulakov, M. P. (1991). *Supercond. Phys. Chem. Tech.* **4**, 237–246.
- Ogborne, D. M., Weller, M. T. & Lanchester, P. C. (1992). *Physica (Utrecht)*, **C200**, 207–214.
- Onoda, M., Kondoh, S., Fukuda, K. & Sato, M. (1988). *Jpn. J. Appl. Phys.* **27**, L1234–L1236.
- Park, C. & Snyder, R. L. (1995). *J. Am. Ceram. Soc.* **78**, 3171–3194.
- Rao, C. N. R. & Ganguli, A. K. (1995). *Acta Cryst.* **B51**, 604–618.
- Sasaki, S., Kawaguchi, K. & Nakao, M. (1992). *Jpn. J. Appl. Phys.* **31**, L467–L470.
- Schwer, H., Karpinski, J., Lesne, L., Rossel, C., Morawski, A., Lada, T. & Paszewin, A. (1995). *Physica (Utrecht)*, **C254**, 7–14.
- Sendyka, T. R., Dmowski, W., Egami, T., Seiji, N., Yamauchi, H. & Tanaka, S. (1995). *Phys. Rev. B*, **51**, 6747–6750.
- Sharma, R. P., Rotella, F. J., Jorgensen, J. D. & Rehn, L. E. (1991). *Physica (Utrecht)*, **C174**, 409–422.
- Sharma, R. P., Venkatesan, T., Zhang, Z. H., Liu, J. R., Chu, R. & Chu, W. K. (1996). *Phys. Rev. Lett.* **77**, 4624–4627.
- Srinivasan, R., Girirajan, K. S., Ganesan, V., Radhakrishnan, V. & Subba Rao, G. V. (1988). *Phys. Rev. B*, **38**, 889–893.
- Subramanian, M. A., Calabrese, J. C., Torardi, C. C., Gopalakrishnan, J., Askew, T. R., Flippen, R. B., Morrissey, K. J., Chowdhry, U. & Sleight, A. W. (1988). *Nature (London)*, **332**, 420–422.
- Toby, B. H., Egami, T., Jorgensen, J. D. & Subramanian, M. A. (1990). *Phys. Rev. Lett.* **64**, 2414–2417.
- Trounov, V. A., Kaganovich, T. Yu., Fischer, P., Kaldis, E., Karpinski, J. & Jilek, E. (1994). *Physica (Utrecht)*, **C227**, 285–290.