

Fig. 1. Stereoview of the environment of a (central) nickel ion in the hexaaquanickel(II) chlorate structure from a direction nearly along the x axis (with the z axis vertical). The 12 strong hydrogen bonds to the chlorate ions from the six water molecules associated with this central nickel ion are shown. Drawn using ORTEPII (Johnson, 1971). Thermal ellipsoids are drawn at 50% probability for all atoms except H, for which they have been set artificially small.

rate hydrates, Yü & Beevers (1936) have determined the structure of $\text{Zn}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$, which is isomorphic and strikingly similar (with respect to the heavy atoms) to that determined here for $[\text{Ni}(\text{H}_2\text{O})_6]-(\text{ClO}_3)_2$. A helpful view of a unit-cell projection is presented in their Fig. 3, while their Fig. 5 presents photographs of their three-dimensional model of a unit cell suitable for stereographic viewing.

In Table 4 we have tabulated previously published representative results for Ni—O coordination polyhedra and chlorate ions for comparison with the values determined in this study.

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Untwinned Single Crystals of the High-Temperature Superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$

BY K. BRODT AND H. FUESS

Institut für Kristallographie und Mineralogie der Universität Frankfurt-am-Main, Senckenberganlage 30, Frankfurt-am-Main, Federal Republic of Germany

E. F. PAULUS

Hoechst AG, 623 Frankfurt-am-Main 80, Federal Republic of Germany

AND W. ASSMUS AND J. KOWALEWSKI

Physikalisches Institut der Universität Frankfurt-am-Main, Robert-Mayer-Strasse 2–4, Frankfurt-am-Main, Federal Republic of Germany

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Abstract. $\text{YBa}_2\text{Cu}_3-0.06(1)\text{O}_{7-0.18(2)}$, $M_r = 659.5$, orthorhombic, $Pmmm$, $a = 3.836(1)$, $b = 3.883(1)$, $c = 11.686(1)$ Å, $V = 174.07$ Å³, $Z = 1$, $F(000) = 290.82$, $D_x = 6.36$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 28.48$ mm⁻¹, $T = 295$ K, $R = 0.0495$, $wR = 0.0341$ for 1342 unique diffractometer data [$F^2 > 1\sigma(F^2)$] up

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to $(\sin\theta)/\lambda = 1.15 \text{ \AA}^{-1}$, only 3 reflections had intensities smaller than 1 standard deviation. The crystal of dimensions $0.1 \times 0.075 \times 0.025 \text{ mm}$ was apparently untwinned. Precise positional and thermal parameters were obtained. The exact formula is $\text{YBa}_2\text{Cu}_2\text{-Cu}_{0.94}\text{O}_4\text{O}_{1.84}\text{O}_{0.83}\text{O}_{0.15}$.

Introduction. The compound $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ melts incongruently at 1270 K; at 970 K the non-superconducting tetragonal phase transforms to the orthorhombic one (Hewat, Capponi, Chaillout, Marezio & Hewat, 1987); crystals in this phase are normally twinned (Roth, Ewert, Heger, Hervieu, Michel, Raveau, D'Yvoire & Revcolevschi, 1987). The structures reported so far (*e.g.* Garbaskas, Arendt & Kasper, 1987; Miraglia, Beech, Santoro, Tran Qui, Sunshine & Murphy, 1987; Randsepp, Hawthorne, Zhou, Maartense, Morrish & Luo, 1987; Hewat *et al.*, 1987; Sato, Nakada, Kohara & Oda, 1988; Takeya & Takei, 1988; Paulus, Kämpf, Schmidt & Höhle, 1988) were obtained from twinned specimens or from powders. When the structure determination described here was completed (Paulus, Brodt, Fuess, Assmus & Kowalewski, 1988), we learned of the work of Simon, Köhler, Borrmann, Gegenheimer & Kremer (1989), who reported the structure determination from untwinned crystals. Raman spectroscopy on a $40 \mu\text{m}$ untwinned single crystal was reported from the same group (Thomsen, Cardona, Gegenheimer, Liu & Simon, 1988).

It is not possible to determine unambiguously the site occupation factors (s.o.f.) of the oxygen positions O(4) and O(5) from twinned crystals (Paulus, Kämpf, Schmidt & Höhle, 1988; Paulus, Fuess, Pabst, Assmus, Schmidt & Höhle, 1988), because the twin domains are related by (110). Furthermore, most previous structure determinations were hampered by negative or very small temperature coefficients. When it became apparent from precession photographs that we had obtained by chance an untwinned crystal of high quality, we decided to collect a full data set.

Experimental. The superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ was produced by sintering Y_2O_3 , BaO and CuO powder. It was ground and mixed with the flux medium BaO–CuO of molar ratio 1:2 (Kaiser, Holtzberg, Chisholm & Wortington, 1987; Balestrino, Barbanera & Paroli, 1987; Scheel & Licci, 1987). The solution (15 to 30% of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$) was heated in a crucible of alumina to 1270 K and left there for two days in air atmosphere. It was cooled subsequently at a rate of 4 K h^{-1} to 1070 K and at a rate of 10 K h^{-1} to 670 K. The cubic crystals with dimensions of 1.5 mm were not superconducting at 77 K. They had to be annealed at 1170 K and cooled at a slow rate to 670 K in an oxygen atmosphere of

2 bar in order to acquire a T_c of 87 K (Lotter, Wittig, Assmus & Kowalewski, 1989).

A splinter of one of these crystals with dimensions $0.1 \times 0.075 \times 0.025 \text{ mm}$ was sealed in a Lindemann-glass capillary; this specimen was, however, too small for a direct measurement of T_c , which was therefore taken as 87 K as determined on the larger crystal. The aluminium content, imported from the crucible out of alumina, was determined from another (twinned) splinter of the same cubic crystal by atomic absorption spectroscopy (GFAAS, Hitachi atomic absorption spectrometer 180/80) to be $0.1 + 0.05 \text{ w\%}$. It was, however, possible to perform EDX measurements (Cambridge Stereoscan 150 S; EDX supplement: Kevex Corp., Foster City, Calif.) on the surface of the splinter under investigation (Fig. 1.). The broken line presents the results of the overwhelming 'clean' part of the crystal, whereas the full line shows the composition of particles on the surface of the crystal. These very small particles consist apparently of a kind of Na–Al silicate, whose components come from the crucible material or other impurities. The composition of the matrix, of course, can still be seen in the spectrum of the particles.

The profiles of all reflections registered showed a peak shape characteristic of untwinned crystals. In Fig. 2 some profiles are displayed and compared with profiles of a twinned crystal (Paulus, Kämpf, Schmidt & Höhle, 1988). Plots of the profiles of more than 20 further reflections have been deposited together with the profiles of a twinned splinter of the same cubic 'crystal'.*

25 reflections ($2\theta > 35^\circ$) were used for the cell refinement; one standard reflection ($1\bar{2}3$); 9903 meas-

* The profiles of more than 20 reflections and lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52295 (66 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

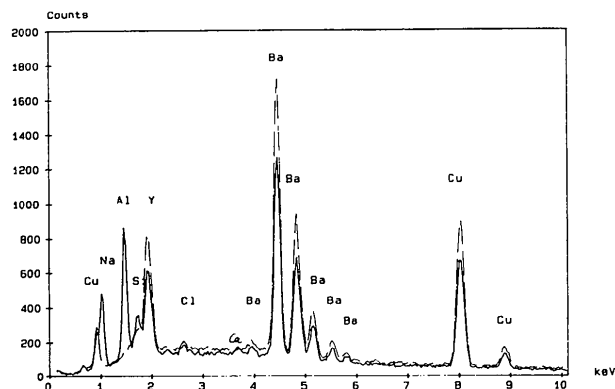


Fig. 1. EDX spectra of two characteristic spots of the surface of the crystal. 'Clean' parts of the crystal are indicated by the broken line; 'dusty' parts of the crystal by the full line.

ured reflections ($h = -8$ to $+8$, $k = -8$ to $+8$, $l = -26$ to $+26$) resulted in 1342 observed [intensity $I > \sigma(I)$] unique reflections after an empirical absorption correction according to the ψ method (Sheldrick, 1983); extinction correction (Sheldrick, 1983); $R_{\text{int}} = 0.039$; only three reflections were unobserved; Nicolet R3 computer-controlled diffractometer, $2\theta/\theta$ scan, $2\theta_{\text{max}} = 110^\circ$, 3° min^{-1} . Starting atomic coordinates were taken from Paulus, Kämpf, Schmidt & Hönle (1988), scattering factors and f' , f'' from *International Tables for X-ray Crystallography* (1974). The parameter refinement was performed by the cascade method (Sheldrick, 1983), minimization of $\sum w(F_o - F_c)$. Anisotropic temperature factors were refined for all atoms except O(5). The weighting scheme $w = 1/\sigma(F)$, where $\sigma(F)$ is from counting statistics, 35 parameters, 1307 degrees of freedom. Tentative least-squares calculations at the very beginning of the parameter refinement showed that only the site occupation factors of Cu(1), O(1), O(4) and O(5) are significantly different from unity. They were refined together with all the other atomic parameters. The proof that the correlation with the appropriate tem-

perature coefficients is not too strong was that there was no change of the parameters when the refinement was continued fixing the site occupation factors or the temperature coefficients. $R = 0.0495$, $wR = 0.0341$. All calculations were performed with a Nova 3/12 computer and *SHELXTL* (Sheldrick, 1983). Atomic coordinates are given in Table 1, and a view of the crystal structure is provided in Fig. 3.

Discussion. The site occupation factors of O(1), O(4) and Cu(1) are 6 to 15 standard deviations different from unity, and significantly indicate vacancies. The site occupation factor of O(5) is 10 standard deviations larger than zero. The complete formula is then YBa₂Cu₂Cu_{0.94}O₄O_{1.84}O_{0.83}O_{0.15}. If it is accepted that the valence state of Cu(1) is 3 and that of Cu(2) is 2, then we have electroneutrality without introducing 'broken' oxidation numbers.

There are no significant differences of the interatomic distances compared with those in twinned crystals, which were investigated earlier (Paulus, Kämpf, Schmidt & Hönle, 1988; Paulus, Fuess, Pabst, Assmus, Schmidt & Hönle, 1988). The stand-

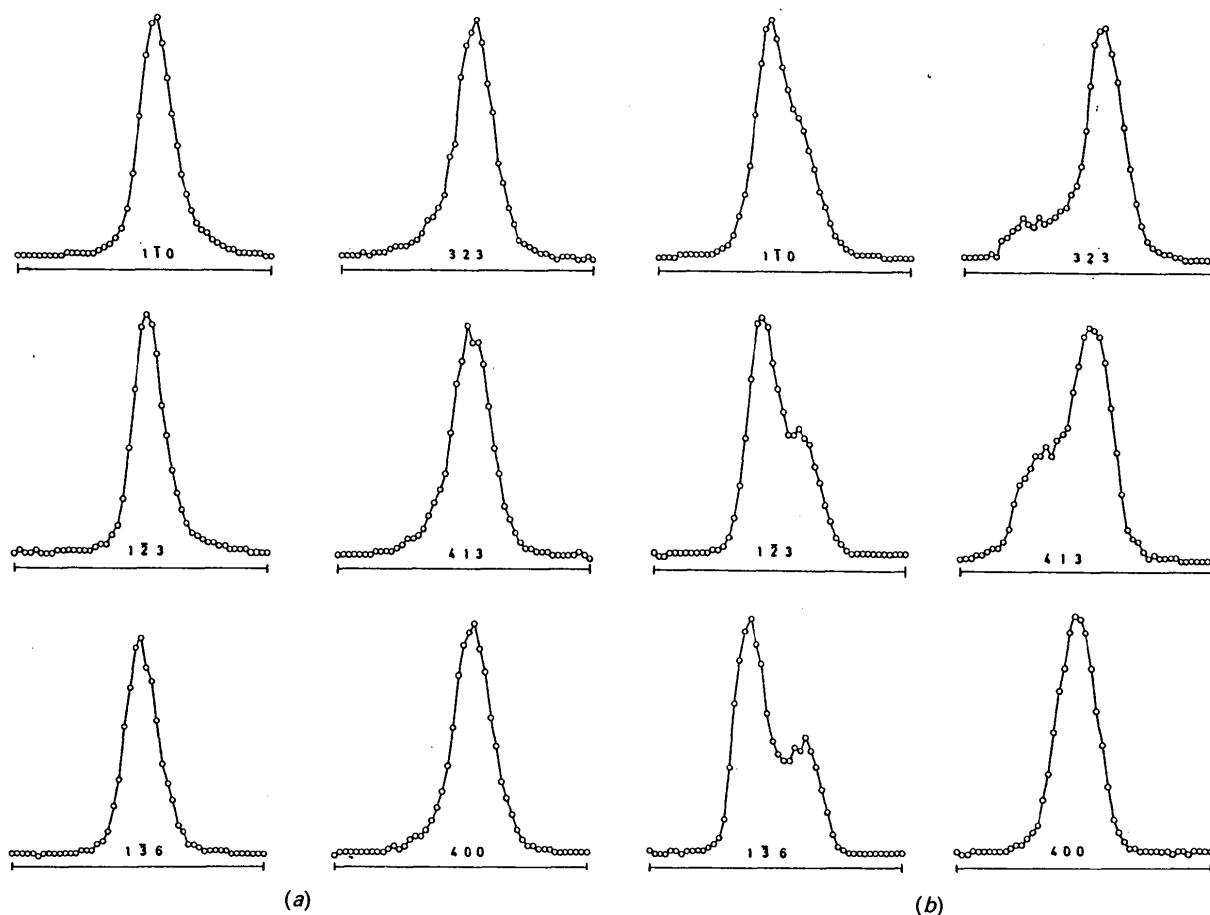


Fig. 2. Profiles of a few reflections of (a) the untwinned single crystal and (b) a twinned crystal. Scan ranges are 1.94° in ω .

Table 1. Atomic coordinates, anisotropic and equivalent isotropic temperature coefficients, and site occupation factors

The atomic coordinates are given in units of the lattice constants; the isotropic temperature coefficients (in Å²) were calculated from the anisotropic ones after the last least-squares cycle. E.s.d.'s are in parentheses.

	x	y	z	U ₁₁	U ₂₂	U ₃₃	U _{eq} (Å ²)	S.o.f.
Y(1)	0.50	0.50	0.5000	0.0060 (2)	0.0049 (2)	0.0051 (2)	0.0053 (1)	1.0000
Ba(1)	0.50	0.50	0.18434 (2)	0.0100 (1)	0.0069 (1)	0.0076 (1)	0.0082 (1)	1.0000
Cu(1)	0.00	0.00	0.0000	0.0097 (3)	0.0077 (3)	0.0045 (2)	0.0073 (2)	0.941 (4)
Cu(2)	0.00	0.00	0.35588 (5)	0.0052 (1)	0.0043 (2)	0.0083 (3)	0.0060 (1)	1.0000
O(1)	0.00	0.00	0.1580 (3)	0.014 (1)	0.011 (1)	0.007 (1)	0.0106 (7)	0.921 (13)
O(2)	0.50	0.00	0.3786 (3)	0.006 (1)	0.006 (1)	0.010 (1)	0.0073 (6)	1.0000
O(3)	0.00	0.50	0.3786 (3)	0.007 (1)	0.004 (1)	0.010 (1)	0.0070 (5)	1.0000
O(4)	0.00	0.50	0.0000	0.032 (4)	0.011 (3)	0.013 (3)	0.019 (2)	0.83 (2)
O(5)	0.50	0.00	0.0000				0.018 (7)	0.15 (2)

The anisotropic temperature factor is defined by $\exp\{-8\pi^2[(ha^*/2)^2U_{11} + (kb^*/2)^2U_{22} + (lc^*/2)^2U_{33} + (2hka^*b^*)/4U_{12} + (2hla^*c^*)/4U_{13} + (2klb^*c^*)/4U_{23}]\}$.

ard deviations are, however, significantly smaller. The cell constants correspond to those of phase *D* (Fjellvåg, Karen & Kjekshus, 1987). They are, however, slightly smaller, which is attributed to the good quality of the crystal giving reflections of relatively high intensities up to large diffraction angles ($2\theta_{\max} = 110^\circ$).

The small site occupation factor of O(5) may be the result of a certain amount of twinning. A twin domain of 15% of the volume should manifest itself in the reflection profiles. No indication of a second crystal could be detected in any reflection profile (Fig. 2). Different site occupation factors for O(4) and O(5) were reported from *in situ* neutron powder diffraction between 800 and 1000 K (Jorgensen *et al.*, 1987). It seems that this state can, as in our case, be partly frozen in at room temperature. Fig. 7 of that paper does not exclude the possibility that there is some oxygen at O(5), perhaps also at room temperature.

When our work was partly published (Paulus, Brodt, Fuess, Assmus & Kowalewski, 1988), we learned of the structure analysis of another untwinned single crystal of YBa₂Cu₃O_{7-x} (Simon, Köhler, Borrmann, Gegenheimer & Kremer, 1989). The analysis was done at different temperatures. It could be shown that there are no vacancies at the Cu positions and that there is no oxygen at O(5). It was pointed out that Cu^{III} can be partially substituted by Al^{III}. This substitution may lead to an apparent site occupation factor of Cu(1) as found in our refinement. The results of atomic absorption spectroscopy on the same material indicated 0.10 (5)% Al, an amount which could indeed explain the deviation of the site occupation factor from unity. The EDX results on the crystal under investigation showed, however, that Al (and Si) are concentrated in some small regions whereas the overwhelming part of the crystal does not contain any Al. These results lead us to conclude that the substitution of Cu^{III} by Al^{III} is fairly unlikely. The occupation number of

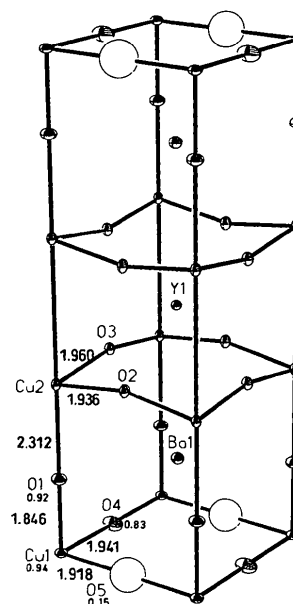


Fig. 3. Crystal structure with selected interatomic distances in Å. The site occupation factors different from 1 are also given.

Cu(1) corresponds to vacancies in the appropriate oxygen positions.

Hönle & von Schnering (1988) demonstrated that intensity measurements cannot distinguish unambiguously between twinning by pseudo-merohedry and statistical occupation of the O(4) and O(5) positions. Consequently, despite the almost perfect peak profiles observed in our study, we cannot exclude the presence of a small amount of twinning in our specimen. The different amount of oxygen observed by various authors in the O(5) position may therefore be either a result of twinning or reflect different treatments of the samples under investigation.

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Redetermination of the Structure of Caesium Hydrogensulfate

BY K. ITOH, T. UKEDA, T. OZAKI AND E. NAKAMURA

Department of Materials Science, Faculty of Science, Hiroshima University, Hiroshima 730, Japan

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Abstract. CsHSO₄, $M_r = 229.98$, monoclinic, $P2_1/c$, $a = 8.214$ (2), $b = 5.809$ (2), $c = 10.984$ (2) Å, $\beta = 119.39$ (2)°, $V = 456.7$ (2) Å³, $Z = 4$, $D_x = 3.346$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 8.318$ mm⁻¹, $F(000) = 416$, $R = 0.057$, $wR = 0.062$, 2172 unique reflections, $T = 296$ K (low-temperature phase). The structure deviates slightly from the previously reported structure with space group $P2_1/m$, and $Z = 2$. The unit cell is composed of two pseudocells. Two kinds of similar hydrogen-bonded chains, in which hydrogens are located opposite each other with respect to the center of the hydrogen bond, run along the b axis one dimensionally.

Introduction. It is known that many compounds with the formula $AHBO_4$ ($A =$ monovalent atoms or groups, $B =$ S, Se) exhibit the following properties: (1) they undergo (successive) phase transitions, (2) a good number of them display superionic character in

the high-temperature phase, (3) the phase transition is often irreversible, and (4) moisture sometimes affects the character of the phase transition. CsHSO₄, a typical compound of this type, undergoes successive phase transitions from a low-temperature phase to an intermediate phase in the temperature range from 333 to 370 K on heating (Belushkin, Natkaniec, Pakida, Shuvalov & Wasicki, 1987), and then to a superionic high-temperature phase at $T_i = 410$ –414 K (Komukae, Osaka, Makita, Ozaki, Itoh & Nakamura, 1981; Baranov, Fedosyuk, Schagina & Shuvalov, 1984). The low-temperature phase, however, does not appear on cooling the high-temperature phase (Belushkin *et al.*, 1987). The X-ray structure analysis has been carried out at room temperature on the low-temperature phase (Itoh, Ozaki & Nakamura, 1981). According to the aforementioned work, the space group of CsHSO₄ is $P2_1/m$ with unit-cell parameters $a = 7.304$, $b = 5.810$,