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X-ray Diffraction Study of Nd_2CuO_4 Single Crystals at 20 K

I. P. MAKAROVA,[a] V. I. SIMONOV,[a] M. K. BLOMBERG[b] AND M. J. MERISALO[b]

[a]*Institute of Crystallography, Academy of Sciences, Leninsky pr. 59, 117333 Moscow, Russia, and* [b]*Department of Physics, PO Box 9, FIN-00014 University of Helsinki, Finland*

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Abstract

Single crystals of Nd_2CuO_4, a parent compound for the electron-doped high-T_c superconductors, have been studied using X-ray diffraction data collected at 20 K. Structure refinements indicated that the specimen was nonstoichiometric, with the approximate formula $Nd_{1.89}CuO_{3.85}$. Difference Fourier maps showed significant residual peaks around the Cu and Nd atoms. The residual density around the Cu atom had features characteristic of the valence state +2. Part of the nonspherical effects observed around the Nd atom could be described using the Gram–Charlier series expansion of the Gaussian density function, indicating either static or dynamic displacements of this atom, while part of the residual density was attributed to bonding effects. The bonding of the O(1) atom, located in the plane of the Cu atoms, was found to be different from the bonding of the O(2) atom, situated between the Cu—O(1) layers.

1. Introduction

Nd_2CuO_4 is a parent structure for the electron-doped high-T_c superconductors. Substitution of Nd by other lanthanides and reduction of the oxygen content can lead to the appearance of superconductivity (Tokura, Takagi & Uchida, 1989). Hall-effect measurements (Takagi, Uchida & Tokura, 1989) and photoelectron spectroscopy (Uji, Shimoda & Aoki, 1989; Grassmann, Ströbel, Klauda, Schlötterer & Saemann-Ischenko, 1989) have shown that charge carriers in these compounds are electrons. The highest T_c, 24 K, has been observed in the (Nd,Ce) system by Takagi *et al.* (1989).

The crystal structure of Nd_2CuO_4 was determined by Müller-Buschbaum & Wollschläger (1975) and the $Nd_{2-x}Ce_xCuO_{4-\delta}$ structure was refined from X-ray and neutron data on powder and single crystal specimens by other groups (Izumi, Matsui, Takagi, Uchida, Tokura & Asano, 1989; Paulus, Yehia, Fuess, Rodriguez, Vogt, Ströbel, Klauda & Saemann-Ischenko, 1990; Galez, Schweiss, Collin & Bellissent, 1990; Kajitani, Hiraga, Hosoya, Fukuda, Oh-ishi, Kikuchi, Syono, Tomiyoshi, Takahashi & Muto, 1990; Marin, Henry & Boucherle, 1993).

The structure of Nd_2CuO_4 is shown in Fig. 1. It differs from the structure of the first hole-doped high-T_c superconductor $(La,Ba)_2CuO_4$ in the oxygen coordination of the lanthanide atoms. All high-T_c superconductors contain square-planar CuO_2 nets as a common structural element. In $(La,Ba)_2CuO_4$ the squares of the main net are completed to elongated CuO_6 octahedra by O atoms located above and beneath the Cu atom, and the La and Ba atoms have ninefold coordinations. In Nd_2CuO_4 the Cu atom remains coordinated by a flat oxygen square, CuO_4, and the Nd atom has an almost cubic eightfold coordination. The different coordination of the Cu atom – the almost octahedral or pyramidal coordination in the hole-doped compounds and the square coordination in the electron-doped compounds – is an important structural feature of the high-T_c superconductors.

In spite of much attention to the high-T_c superconductors since their discovery (Bednorz & Müller, 1986), the mechanism of high-temperature superconductivity has not yet been understood. The properties of these compounds are due to the features of the electronic states of atoms and investigations of the electron density could help to explain the connection between the structure and the properties of high-T_c superconductors.

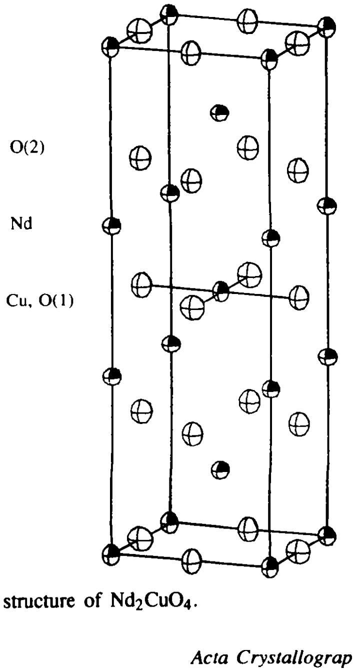

Fig. 1. Crystal structure of Nd_2CuO_4.

The electron deformation-density distribution in Nd_2CuO_4 at 293 K was obtained earlier by Makarova, Molchanov, Tamazyan, Simonov, Gamaunov, Ivanov & Osiko (1993). For a careful comparison with the doped specimens (Makarova, Bram, Markl, Gamaunov, Ivanov, Tamazyan, Röhner, Burzlaff, Saemann-Ischenko, Simonov & Osiko, 1994), there is a need for low-temperature data on the parent structure Nd_2CuO_4. It is also important to confirm the previously obtained results by collecting data on another device. Therefore, we have carried out an investigation of the same single crystal sample at 20 K.

2. Experimental methods

Nd_2CuO_4 crystals were grown by spontaneous crystallization from solution in melt (Gamaunov, Ivanov, Osiko & Tatarintsev, 1991). The measurements were carried out on a specimen shaped into a sphere. The sample was tested previously for the absence of violations of the *I4/mmm* symmetry. The absence of twinning was confirmed using two-dimensional scanning of selected areas of the reciprocal space. In order to prevent the influence of stress on the crystal at low temperatures, the specimen was mounted on a quartz thread using beeswax.

Diffraction data were collected at 20 K on a Huber 5042 four-circle diffractometer equipped with a Displex 202 two-stage closed-cycle helium cryostat. The stability of the measurement temperature was ±0.3 K. Palladium-filtered Ag $K\bar{\alpha}$ radiation was employed. The change in the crystal positioning, induced by the temperature lowering, was analyzed and corrected by centering a test reflection at several equivalent positions. The lattice parameters were determined by least-squares fitting of the setting angles of 22 reflections with $46 < 2\theta < 50°$, centered at both positive and negative values of 2θ.

The intensity data were measured using coupled ω–2θ scanning. In order to reduce effects caused by instrumental instabilities, the total measurement time was limited. Since a great number of symmetry equivalents (eight reflections per unique reflection) was preferred, the maximum $\sin\theta/\lambda$ was restricted to the relatively low value of 0.90 $Å^{-1}$.

The intensity of one standard reflection (006) was monitored every 50 reflections during the data collection. This reflection was chosen due to its high sensitivity to changes in the crystal height, which may be induced by temperature or pressure changes in the measurement chamber during the experiment. No systematic time dependence of this intensity was observed over the whole data collection period. In addition, the crystal orientation matrix was checked between the measurements of each independent set of reflections. No changes in the crystal orientation were observed.

Intensity data were reduced to $|F|^2$ values with the programs *REFPK* and *BGLP* (Blessing, 1987), which use the algorithm presented by Lehmann & Larsen (1974) for determination of the background level and apply corrections for Lorentz and polarization effects. Absorption corrections for the spherical sample were calculated by interpolating from the values tabulated by Weber (1969). The data were also corrected for absorption in the cylindrical vacuum cans consisting of beryllium and surrounding the sample.

Averaging of the intensities of the symmetrically equivalent reflections led to the value 2.17% of the (conventional) internal agreement factor, defined as

$$R_{\text{int,c}} = \sum_k \sum_j |I_{k,j} - \bar{I}_k| / \sum_k \sum_j I_{k,j}, \qquad (1)$$

where $I_{k,j}$ is the jth intensity measurement in a group k of symmetrically equivalent reflections and $\bar{I}_k$ is the averaged intensity of the group k, forming a unique reflection. After rejecting 85 discordant reflections, the factor decreased to the value 1.88%. The agreement factor presented in Table 1 is defined as in the previous study of the room-temperature data (Makarova *et al.*, 1993)

$$R^2_{\text{int}} = \sum_k \sum_j (I_{k,j} - \bar{I}_k)^2 / \sum_k \sum_j I^2_{k,j}. \qquad (2)$$

The values for this factor were 3.17 (all measured reflections included) and 2.29% (outliers rejected). The rejected reflections were mainly weak and had higher intensity than the other agreeing equivalents, which may be an indication of multiple scattering effects.

The main crystallographic characteristics are listed in Table 1. For comparison, the data measured at 293 K (Makarova *et al.*, 1993) are included.*

3. Structure refinement

The structure model was refined by a full-matrix least-squares method using the program package *PROMETHEUS* (Zucker, Perenthaler, Kuhs, Bachmann & Schulz, 1983). The atomic scattering factors and dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The extinction corrections were carried out using the program *JANA* (Petricek, Coppens & Becker, 1985). The room-temperature structure (Makarova *et al.*, 1993) was taken as the initial model of the Nd_2CuO_4 structure at 20 K.

The extinction model was selected by comparing the agreement between the observed and calculated structure factors obtained for different models. The best extinction

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* A list of structure factors has been deposited with the IUCr (Reference: SH0051). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Experimental details*

	293 K	20 K
Crystal data		
Chemical formula	$CuNd_2O_4$	$CuNd_2O_4$
Chemical formula weight	416.02	416.02
Cell setting	Tetragonal	Tetragonal
Space group	$I4/mmm$	$I4/mmm$
a (Å)	3.9488 (3)	3.9379 (2)
c (Å)	12.1869 (9)	12.1400 (6)
V (Å^3)	190.03	188.26
Z	2	2
D_x (Mg m^{-3})	7.27	7.34
Radiation type	Ag $K\overline{\alpha}$	Ag $K\overline{\alpha}$
Wavelength (Å)	0.5609	0.5609
Max. sin θ/λ (Å^{-1})	1.30	0.90
No. of reflections for cell parameters	24	20
θ range (°)	23–25	23–25
μ (mm^{-1})	16.96	17.12
Temperature (K)	293	20
Crystal form	Spherical	Spherical
Crystal diameter (μm)	140 (5)	140 (5)
Crystal color	Black, opaque	Black, opaque
Data Collection		
Diffractometer	Enraf–Nonius CAD-4*F*	Huber 5042
Data collection method	ω–2θ	ω–2θ
Absorption correction	Numerical	Numerical
T_{min}	0.1899	0.1859
T_{max}	0.2405	0.2106
No. of measured reflections	5015	1664
No. of independent reflections	525	208
No. of observed reflections	525	208
R_{int}	0.023	0.031
θ_{max} (°)	47	30
Range of h, k, l	$-10 \rightarrow h \rightarrow 10$ $-10 \rightarrow k \rightarrow 10$ $-31 \rightarrow l \rightarrow 31$	$-7 \rightarrow h \rightarrow 7$ $-7 \rightarrow k \rightarrow 7$ $-21 \rightarrow l \rightarrow 21$
No. of standard reflections	2	1
Frequency of standard reflections	Every hour	Every 50 reflections
Refinement		
Refinement on	F	F
R	0.0070	0.0060
wR	0.0082	0.0076
S	1.84	1.82
No. of reflections used in refinement	484	173
No. of parameters used	18	16
Weighting scheme	$w = 1/\sigma^2(F_O)$	$w = 1/\sigma^2(F_O)$
$(\Delta/\sigma)_{max}$	0.001	0.001
$\Delta\rho_{max}$ (e Å^{-3})	0.95	0.85
$\Delta\rho_{min}$ (e Å^{-3})	-1.21	-0.085
Extinction method	Lorentzian (Becker & Coppens, 1974)	Lorentzian (Becker & Coppens, 1974)
Extinction coefficient	0.43	0.44
$g_{11} = g_{22}$	0.070 (9)	0.071 (4)
g_{33}	0.019 (3)	0.019 (1)
Source of atomic scattering factors	*International Tables for X-ray Crystallography* (1974, Vol. IV)	*International Tables for X-ray Crystallography* (1974, Vol. IV)
Computer programs		
Data collection	Enraf–Nonius	MAD (ILL, Grenoble)
Cell refinement	Enraf–Nonius	RAFIN (ILL, Grenoble)
Data reduction	Enraf–Nonius	REFPK, BGLP (Blessing, 1987)
Structure refinement	*PROMETHEUS* (Zucker *et al.*, 1983)	*PROMETHEUS* (Zucker *et al.*, 1983)

model, according to the formalism of Becker & Coppens (1974), was the Lorentzian anisotropic mosaic distribution (type I). The four strongest reflections (103, 110, 200 and 220), with the extinction factor $0.44 < y < 0.64$ (with respect to $|F|^2$), were excluded from the final structure refinement.

After the first refinements it was observed that most of the reflections having large values of $|F_{obs} - F_{calc}|/\sigma(F)$ were weak reflections with $|F_{obs}|$ systematically greater than $|F_{calc}|$. This indicates that even after rejecting the most discordant reflections in the averaging process, some of the reflections are still affected by multiple scattering. Therefore, 31 such reflections (mainly with $l = 2$, 15, 18 or 19) were excluded from further refinements.

Since superconductivity in $Nd_{2-x}Ce_xCuO_{4-y}$ appears only in specimens with reduced oxygen content

(Uchida, 1990), determination of the oxygen site occupancies is of great importance. Suzuki, Kishio, Hasegawa & Kitazawa (1990) obtained oxygen deficiencies from 0.008 to 0.04 in $Nd_2CuO_{4-\delta}$ and $Nd_{2-x}Ce_xCuO_{4-\delta}$ powder samples using thermogravimetry and chemical titration analysis. Galez *et al.* (1990) observed a significant copper deficiency in $Nd_{2-x}Ce_xCuO_{4-y}$ single crystals. They obtained Cu occupancies of 0.937 (12)–0.964 (9) and concluded that the Cu content is related to the preparation method. From neutron diffraction data on a large specimen of Nd_2CuO_4, they found both oxygen sites to be under-occupied [$q_{O(1)} = 0.978\,(8)$, $q_{O(2)} = 0.971\,(8)$], while the Cu position had a full occupancy. In a single-crystal neutron diffraction study on the structure of Nd_2CuO_4, Marin *et al.* (1993) obtained the oxygen stoichiometry of 3.94 (5) in the initial compound and 3.89 (4) in the reduced sample. According to their results, the oxygen deficiency of 0.06 in the O(2) position remained unaffected during the reduction treatment, while oxygen removal of 0.05 occurred in the O(1) site. Nonstoichiometry of Nd or Cu was not observed.

In the specimen under study, the refined site occupancies indicated deficiency in the neodymium and oxygen [O(1)] contents. The neodymium occupancy q_{Nd} obtained from the 20 K data corresponds well to the room-temperature value (see Table 2), while the oxygen occupancy $q_{O(1)}$ seems to be slightly smaller than the corresponding room-temperature value. No deviations from the full occupancy, within the experimental accuracy, were observed for the O(2) position. Attempts to refine occupancies for the Cu and O sites, keeping q_{Nd} fixed to full occupancy, led to over-occupancy of Cu, which would imply a partial replacement of Cu atoms by Nd. However, due to the square coordination of the copper site, this is not very probable. Thus, the final refinements were carried out keeping q_{Cu} fixed to full occupancy. No constraints for charge neutrality of the compound were included in the refinements. According to the obtained results, the approximate formula of the specimen compound is $Nd_{1.89}CuO_{3.85}$.

The significance of the observed deviations from full occupancies and the possible influence of valence states were analyzed by high-angle refinements of the room-temperature data using different minimum values of $\sin\theta/\lambda$ (Makarova *et al.*, 1993). A tendency to slightly increasing values of q with increasing cut-off limit was observed, especially for $q_{O(1)}$. This fact may partially explain the small discrepancy observed in the oxygen occupancies $q_{O(1)}$ at the two different temperatures, since the maximum $\sin\theta/\lambda$ of the 20 K data set was lower than that of the 293 K data. However, increasing the cut-off limit did not change the values of the refined site occupancies by more than three standard deviations. Furthermore, regardless of the overall defect content, the oxygen deficiency correlated with the neodymium deficiency, retaining the electric charge neutrality of the compound.

Table 2. *Refined structure parameters for Nd_2CuO_4*

Atom positions: Nd at 4(*e*) (0,0,*z*); Cu at 2(*a*) (0,0,0); O(1) at 4(*c*) (0,$\frac{1}{2}$,0); O(2) at 4(*d*) (0,$\frac{1}{2}$,$\frac{1}{4}$). Occupancy parameters: q. Thermal parameters U_{ij} (Å^2) are defined by the temperature-factor equation $T_0 = \exp(-2\pi^2 \sum_i \sum_j h_i h_j a_i^* a_j^* U_{ij})$. The equivalent isotropic thermal parameters (in Å^2) are $B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$. The temperature factor with allowance for anharmonicity is defined as $T = T_0\{1 + [(2\pi i)^3/3!] c_{jkl} h_j h_k h_l + [(2\pi i)^4/4!] d_{jklm} h_j h_k h_l h_m + \ldots\}$. The presented values of the parameters d_{jklm} are multiplied by 10^6. The estimated standard deviations are given, in parentheses, on the last quoted place. The values presented without e.s.d.'s were fixed.

		293 K	20 K
Nd	q	0.945 (1)	0.944 (3)
	z	0.351056 (3)	0.35124 (1)
	$U_{11} = U_{22}$	0.00585 (2)	0.00133 (4)
	U_{33}	0.00493 (3)	0.00097 (5)
	$d_{1111} = d_{2222}$	0.153 (7)	0.14 (2)
	d_{3333}	−0.00093 (8)	0
	d_{1122}	0.041 (3)	0
	B_{eq}	0.438 (2)	0.095 (3)
Cu	q	1	1
	$U_{11} = U_{22}$	0.00497 (2)	0.00126 (8)
	U_{33}	0.00749 (4)	0.00234 (15)
	B_{eq}	0.459 (3)	0.128 (5)
O(1)	q	0.925 (3)	0.89 (2)
	U_{11}	0.0107 (2)	0.0049 (7)
	U_{22}	0.0061 (2)	0.0020 (7)
	U_{33}	0.0108 (2)	0.0030 (7)
	B_{eq}	0.72 (1)	0.26 (2)
O(2)	q	1	1
	$U_{11} = U_{22}$	0.0074 (1)	0.0042 (5)
	U_{33}	0.0100 (2)	0.0057 (7)
	B_{eq}	0.653 (8)	0.37 (2)

The possibility of the presence of an interstitial oxygen site was checked according to the proposal of Tarascon, Wang, Greene, Ramesh, Bagley, Hull, Miceli, Wang, Brawner & Ong (1989). The refined occupancy of the position $(0,0,z_{O(3)})$ was equal to zero, indicating the absence of the apical oxygen, in accordance with the results of Marin *et al.* (1993).

In the difference syntheses of the electron density, constructed using the 293 K data, residual peaks in the density were found near the Nd atom (Makarova *et al.*, 1993). Analysis of the experimental data showed that the main contribution to the formation of these peaks came from high-angle reflections. This indicates that, instead of being related to valence electrons, the residual peaks might be caused by dynamic displacements due to anisotropic anharmonic thermal vibrations or by static displacements of a fraction of the Nd atoms from their average positions. Thus, refinements of the displacement parameters were carried out using the Gram–Charlier temperature-factor formalism. Parameters up to fourth order were included (see Table 2). Taking into account the symmetry restrictions of the Nd-atom position, the refined parameters were c_{333}, $c_{113}(= c_{223})$, $d_{1111}(= d_{2222})$, d_{3333}, d_{1122} and $d_{1133}(= d_{2233})$. After the first refinements it was observed that the (absolute) values

Table 3. *Main interatomic distances (Å) and angles (°) for Nd_2CuO_4*

Estimated standard deviations are given in parentheses.

	293 K	20 K
Nd—O(1^{i})	2.6820 (1)	2.6717 (1)
Nd—O(2)	2.3270 (1)	2.3211 (1)
Nd—Nd^{ii}	3.6303 (3)	3.6119 (2)
Nd—Nd^{iii}	3.7234 (2)	3.7143 (2)
Nd—Cu	4.2783 (3)	4.2641 (2)
Nd—Cu^{iv}	3.3304 (1)	3.3189 (1)
Cu—O(1)	1.9744 (2)	1.9690 (2)
O(1^{i})—Nd—O(2)	74.55 (1)	74.50 (1)
O(1^{i})—Nd—O(1^{v})	94.81 (1)	94.95 (1)
O(1^{i})—Nd—O(1^{vi})	62.74 (1)	62.81 (1)
O(2)—Nd—O(2^{vii})	116.09 (1)	116.05 (1)
O(2)—Nd—O(2^{viii})	73.73 (1)	73.72 (1)

Symmetry codes: (i) $x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (ii) $x, -y, -z+1$; (iii) $x+\frac{1}{2}, -y+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $x+\frac{1}{2}, y+\frac{1}{2}, z+\frac{1}{2}$; (v) $-y+\frac{1}{2}, x-\frac{1}{2}, z+\frac{1}{2}$; (vi) $x-\frac{1}{2}, y-\frac{1}{2}, z+\frac{1}{2}$; (vii) $x, y-1, z$; (viii) x, y, z.

of some of the parameters were smaller than the e.s.d.'s. Since the refinement of these parameters did not decrease the *R* factor, they were excluded from the subsequent refinements (*i.e.* fixed to zero values). From the 293 K data, significant values were obtained for the parameters d_{1111}, d_{3333} and d_{1122}. No significant high-order displacement parameters were obtained for the other atoms of the structure.

For the 20 K data, introduction of the Gram–Charlier fourth-order tensor elements in the Nd-atom temperature factor decreased the *R* factor from 0.83 to 0.78%. According to statistical significance tests (Hamilton, 1965) of the *R* factor ratio on the level 0.005, the improvement in the fit is significant. The only nonzero anharmonic thermal parameter was $d_{1111}(= d_{2222})$ of the Nd atom. Usually anharmonicity drops substantially upon cooling, but the parameter d_{1111} does not essentially change when the temperature of the sample is decreased from 293 to 20 K. The result indicates static displacements of the Nd atom towards the O atoms. However, the experimental data are insufficient for making a unique distinction between various models of disorder or for a precise comparison of the displacement parameters obtained at the two different temperatures.

The final refinement of the 20 K data included the following parameters: scale factor, two extinction parameters, one position parameter (*z* of Nd), 10 displacement parameters [including the parameter $d_{1111}(= d_{2222})$ for the Nd atom] and two occupancy parameters [for the Nd and O(1) atoms].

The fractional atomic coordinates and thermal parameters obtained from the final refinements are given in Table 2. The main interatomic distances and bond angles are listed in Table 3. For comparison, the room-temperature data (Makarova *et al.*, 1993) are included.

4. Residual electron density

The residual electron densities were calculated by *X–X* difference Fourier syntheses as

$$\delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \sum_i \rho_i(\mathbf{r} - \mathbf{r}_i), \tag{3}$$

where $\rho(\mathbf{r})$ is the electron-density distribution in the crystal and $\sum_i \rho_i(\mathbf{r} - \mathbf{r}_i)$ is the sum of electron-density distributions of noninteracting, spherically symmetric atoms. The calculated structure factors for spherical atoms were generated from the structure parameters refined, using the model described above, on the full set of data, since a sufficient amount of high-angle data was not available. Although in the previous room-temperature studies (Makarova *et al.*, 1993, Makarova *et al.*, 1994) the structure parameters refined from the full set of data did not deviate from the high-angle results more than three standard deviations, the parameters obtained from the 20 K data may be slightly more biased.

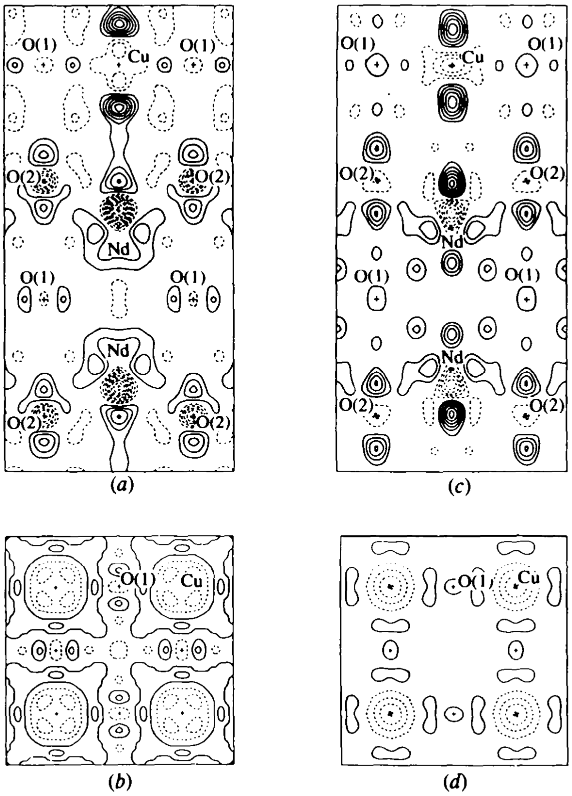
Structure factors for 112 reflections, with $\sin\theta/\lambda < 0.76$ Å^{-1}, were used in the calculation of the electron-density distributions. The cut-off limit was chosen to be the same as used previously for the 293 K data (Makarova *et al.*, 1993). This limit was found to yield the optimum separation of the residual peaks formed by the low- and high-angle data. In comparison to the 293 K data, eight weak reflections were excluded. The electron-density distributions in the planes (010) and (001) are presented in Fig. 2. For comparison, the results for the room-temperature data are included. The errors in the residual peaks of the distributions, estimated according to Stevens & Coppens (1976) using the approximation of Cruickshank (1949), are 0.10 (20 K) and 0.12 e Å^{-3} (293 K).

The formal valence state of copper in Nd_2CuO_4 is +2. Analysis of the maps around the Cu position shows features characteristic for this valence state. The electron-density distribution around the Cu atom is clearly anisotropic at both temperatures. At 20 K the two highest residual peaks of 0.74 e Å^{-3} are located 0.99 Å from the Cu atom along the *z* axis, while at 293 K the corresponding peaks are 0.95 e Å^{-3} in height and their distance from the Cu atom is 1.06 Å. In the (001) plane there are positive peaks located on the four Cu—O(1) bonds. These peaks are diffuse in shape and their height is 0.18 e Å^{-3}. At 293 K the positive residual density is spread around the Cu position without a clear separation between the peaks.

The same type of anisotropy in the electron density around the Cu atom has been reported for another high-temperature superconductor by Sasaki, Inoue, Iyi & Takekawa (1992). They studied the structure of $YBa_2Cu_3O_{6+\delta}$, which has two crystallographically different Cu-atom sites. No residual density was observed around the Cu(1) atom, coordinated to six O atoms, while a pair of residual peaks was observed around the Cu(2) atom, coordinated to five O atoms which form a square plane and a pyramid apex. Both peaks, that in the direction of the apical oxygen and the other in the opposite direction, were located at a distance of 0.92 Å from the Cu atom along the *z* axis. These peaks were considered to arise from localized $3d_{z^2}$ electrons. However, the suggested residual density at the position of hybridized Cu 3*d* and O 2*p* orbitals in the copper–oxygen plane was not observed.

Anisotropic electron densities around Cu have also been found in several studies of other copper compounds. Figgis, Knor, Kucharski & Reynolds (1992) observed positive peaks near the Cu position along the two longest Cu—O bonds in $(ND_4)_2Cu(SO_4)_2.6D_2O$. Tanaka, Konishi & Marumo (1979) investigated $KCuF_3$ crystals with Cu^{2+} ions at pseudotetragonally deformed octahedral sites and observed positive peaks on the longest Cu—F bonds at 0.6 Å from the Cu atom.

The difference Fourier maps (Fig. 2) show significant residual peaks also around the Nd atom. At 20 K there is negative residual density in the Nd position and two positive residual peaks of 0.85 (1.19 Å towards the Cu atom) and 0.50 e Å^{-3} (0.86 Å in the opposite direction). The character of the electron-density distribution is the same at 293 K: negative residual density in the Nd position, a positive peak of 0.59 e Å^{-3} at 1.24 Å towards the Cu position and some diffuse positive density in the opposite direction.



(*a*) (*c*)

(*b*) (*d*)

Fig. 2. The difference Fourier maps (*a*) at 293 K in the (010) plane, (*b*) at 293 K in the (001) plane, (*c*) at 20 K in the (010) plane and (*d*) at 20 K in the (001) plane. Contours of equal densities are drawn at intervals of 0.15 e Å^{-3}. Positive contours are shown by solid lines, negative contours by dashed lines and zero contours are omitted.

According to results using photoelectron spectroscopy (*e.g.* Grassmann *et al.*, 1989), the Nd atom in Nd_2CuO_4 is trivalent and the $4f$-electrons are strongly hybridized with the O 2*p*-states. Our results reveal the redistribution of the valence electrons of the Nd atom due to bonding. It must be emphasized, however, that the interpretation of the difference density in terms of bonding is complicated by the structural disorder of the crystal. The effects of neodymium (and oxygen) vacancies and anharmonic thermal motion or static displacements of atoms cannot unambiguously be separated from effects due to chemical bonding. It is also known that the Gram–Charlier formalism used in X-ray data analysis may successfully represent bonding effects in the valence charge density, in addition to (or instead of) the thermal motion (Mallinson, Koritsanzky, Elkaim, Li & Coppens, 1988), unless atomic asphericity is specifically included in the scattering formalism.

As mentioned above, the analysis of the room-temperature data showed that introduction of the Gram–Charlier formalism in the refinements affected mainly the high-angle data. Although there may still be some contribution of the high-angle data in the (final) residual density, it seems that the peaks near the Nd atom are at least partially due to bonding effects.

A distinction between the bonding of the O(1) atom, located in the plane of the Cu atoms, and the bonding of the O(2) atom, situated between the Cu—O(1) layers, is observed at both temperatures. The positive density spreads from the Nd atom towards the O atoms, with some preference to the direction of the O(2) atom. The difference in the interactions is reflected in the distances Nd—O(1) and Nd—O(2): the former has the value 2.6717 (1) Å, while the latter distance is 2.3211 (1) Å (at 20 K).

Some residual density can also be seen in the vicinity of the O atoms in the (010) plane. At 20 K there are two distinct peaks of 0.56 e Å^{-3} at the distance 0.79 Å from the O(2) position. At 293 K there are similar peaks of 0.46 e Å^{-3} at the distance 0.66 Å and lower positive peaks can be seen near the O(1) atom.

The general features of the electron density are very similar at both temperatures. In order to confirm the obtained results and to distinguish between the various effects in the difference density, *e.g.* by applying a combined Gram–Charlier and multipole refinement, extended low-temperature measurements with a better resolution would be required.

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