Fig. 2. Portion of the structure MoO₂DPO₄.D₂O viewed obliquely to the $y = 0.25$ plane. The hydrogen bonds are represented by broken lines.

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

| Mo—O1 | 2.021 (4) | P—O1 | 1.528 (3) |
|---|---|---|---|
| Mo—O2 | 2.071 (4) | P—O2 | 1.520 (4) |
| Mo—O4 | 1.747 (3) | P—O3 | 1.535 (4) |
| Mo—O5 | 2.271 (6) | O3—D1 | 1.027 (4) |
| Mo—O6 | 1.673 (3) | O5—D2 | 1.019 (6) |
| D1—O4 | 1.750 (4) | O5—D3 | 0.961 (6) |
| D2—O3 | 1.862 (4) | D2—D3 | 1.621 (4) |
| | | | |
| O4—Mo—O6 | 104.1 (9) | D2—O5—D3 | 109.9 (9) |
| O6—Mo—O2 | 95.2 | P—O3—D1 | 107.7 |
| O4—Mo—O5 | 82.1 | O3—D1—O4 | 169.1 |
| O2—Mo—O5 | 78.6 | O5—D2—O3 | 149.5 |
| O1—Mo—O2 | 86.1 | O1—P—O2 | 112.9 |
| O1—Mo—O4 | 91.5 | O1—P—O3 | 114.6 |
| O1—Mo—O5 | 82.5 | O2—P—O3 | 102.5 |
| O1—Mo—O6 | 97.2 | | |

positions determined were significantly displaced from those obtained by Kierkegaard. The Mo environment consists of two short bonds to O4 and O6 typical of a bent molybdenyl group, three normal Mo—O bonds linking to phosphate groups and a more weakly bound D₂O molecule with an Mo—O distance of 2.27 Å. The phosphate group is protonated as is found in other transition-metal phosphates, for example Zr(HPO₄)₂.H₂O. The P—O—H group hydrogen bonds reasonably strongly to O4, which is the sole interaction between the double chains.

The water-molecule geometry is typical for this species in hydrated inorganic compounds; it is held in the $y = 0.25$ plane by a weak hydrogen bond between D2 and O3. The presence of this structural feature fits with the strong absorption at 1620 cm⁻¹ in the IR spectrum which is due to the H₂O symmetric bend.

The coordination geometry of Mo is similar to that observed in molecular Mo[(CH₃)₂NCHO]₂O₂Cl₂ (Flo-rian & Corey, 1968) where a bent MoO₂ group coordinated to oxygen and chlorine in an approximately octahedral environment. In MoO₂DPO₄.D₂O, however, the phosphate groups link the molybdenyl moieties into infinite chains.

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# Redetermination of the Structure of Gd₂CuO₄: A Site Population Analysis

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**Abstract.** In view of recent interest in compounds of the type Ln₂CuO₄ (where Ln = lanthanide), a single-crystal X-ray study has been performed for the redetermination of the structure of Gd₂CuO₄ including a site population analysis. $M_r = 442.04$, tetragonal, $I4/mmm$, $a = 3.892$ (1), $c = 11.878$ (3) Å, $V = 179.91$ Å³, $Z = 2$, $D_x = 8.15$ g cm⁻³, Mo $K\alpha_1$, $\lambda = 0.70926$ Å, $\mu = 423.5$ cm⁻¹, $F(000) = 378$, $T = 295$ K, $R = 2.8\%$, 102 unique reflections used for refinement. The structure consists of a two-dimensional edge-linked square-planar network of [CuO₂]²⁻ groups which are linked by planes of Gd, O and Gd atoms. The oxygen coordination environment around the Gd³⁺ cations is cubic. The

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temperature factor for the O atom in the $[CuO_2]^{2-}$ plane is much larger than those of the other atoms in the system. A least-squares refinement of the population parameters indicates that all sites in $Gd_2CuO_4$ are fully occupied.

**Introduction.** New interest in compounds of the type $Ln_2CuO_4$ (Ln = lanthanide) has been generated by the discovery of high-temperature superconductivity in doped $La_2CuO_4$ (Bednorz & Müller, 1986). The superconducting properties of this system generally have been considered to be dependent on the oxygen stoichiometry of the material and/or a variability of valencies for the Cu atoms (Alp *et al.*, 1987).

In view of the recent attention focused on $Ln_2CuO_4$ materials, we have carried out a redetermination of the structure of $Gd_2CuO_4$. Although a single-crystal structural determination has been reported for $Gd_2CuO_4$ (Grande, Müller-Buschbaum & Schweizer, 1977), the published data indicate only that this system does not possess the $K_2NiF_4$-type structure of $La_2CuO_4$ (Grande, Müller-Buschbaum & Schweizer, 1977), but instead is isostructural with $Nd_2CuO_4$ (Müller-Buschbaum & Wollschläger, 1975). In particular, these data do not contain information on anisotropic thermal parameters nor are statistical uncertainties reported for lattice or positional parameters. As disorder and possible site vacancies have been suggested as contributing to the superconductor phenomena in the related $La_2CuO_4$ system, we have also carried out a site population analysis for $Gd_2CuO_4$.

**Experimental.** *Synthesis.* $Gd_2CuO_4$ single crystals were grown from a PbO-based flux. A mixture of the oxides in the proportions 0·09 $GdO_{3/2}$:0·37 PbO:0·54 CuO was heated in a Pt crucible to 1520 K in air, held 2 h and cooled to 1070 K at 7 K h$^{-1}$, then removed from the furnace. The solidified melt was tapped from the crucible and the cuprate crystals were separated from the CuO—PbO flux using very dilute acetic acid.

*Structure.* A dark parallelepiped-shaped crystal (60 × 80 × 80μm) was cleaved from a larger sample. Unit-cell parameters were derived from a least-squares analysis of 25 reflections (Mo $K\alpha_1$ radiation, $\lambda$ = 0·70926 Å; range, 6 < $\theta$ < 20°) automatically centered on an Enraf–Nonius CAD-4 X-ray diffractometer. Data for four reciprocal-lattice octants ($-5 \le h \le 5$, $-5 \le k \le 5$, and $0 \le l \le 16$) were collected at room temperature over a $2\theta$ scan range of 0·0 to 60·0° (sin $\theta_{max}/\lambda$ = 0·7049 Å$^{-1}$) using a variable-speed $\theta/2\theta$ scan mode and graphite-monochromatized Mo $K\alpha$ radiation. The intensities and orientations of two standard reflections (006 and $\bar{1}\bar{1}4$) were monitored every 2 h of X-ray exposure time and every 200 reflections, respectively. The standard reflections showed no significant intensity fluctuations; reorientation was not required. The intensity data were cor-

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters for* $Gd_2CuO_4$

|        | $x$ | $y$ | $z$ | $U_{eq}(Å^2)^*$ |
|--------|-----|-----|-----|-----|
| Gd(1)  | 0·0 | 0·0 | 0·34916 (7) | 0·79 |
| Cu(1)  | 0·0 | 0·0 | 0·0 | 0·62 |
| O(1)   | 0·0 | 0·5 | 0·25 | 0·9 |
| O(2)   | 0·0 | 0·5 | 0·0 | 2·5 |

\* $U_{eq} = (U_{11} + U_{22} + U_{33})/3$ (×100).

Table 2. *Anisotropic thermal parameters for* $Gd_2CuO_4$ (Å$^2$)

|        | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|--------|------|------|------|------|------|------|
| Gd(1)  | 0·93 (5) | 0·93 (5) | 0·51 (6) | 0·0 | 0·0 | 0·0 |
| Cu(1)  | 0·61 (8) | 0·61 (8) | 0·63 (14) | 0·0 | 0·0 | 0·0 |
| O(1)   | 1·1 (4) | 1·1 (4) | 0·5 (5) | 0·0 | 0·0 | 0·0 |
| O(2)   | 5·5 (11) | 0·9 (6) | 1·2 (7) | 0·0 | 0·0 | 0·0 |

The anisotropic temperature factor is defined by exp $[-2\pi^2(U'_{11}h^2 + U'_{22}k^2 + U'_{33}l^2 + U'_{12}hk + U'_{13}hl + U'_{23}kl)]$ where $U'_{ij} = U_{ij}b_ib_j$ and $U_{ij}$ is multiplied by 100 in the table.

rected for Lorentz and polarization factors. Averaged azimuthal scan intensities for a reflection near $\chi = 90°$ and its Friedel pair measured at 10° increments about $\psi$ showed a variation of $I_{min}/I_{max} = 0·58$. An absorption correction based on these data, multiplied by a spherical correction (0·04 mm), was applied to the intensities. Merging the 616 measured reflections ($R_{int} = 0·029$) gave rise to 102 independent reflections $[I \ge 2\sigma(I)]$ which were used in the structural refinement.

Although normalized structure-factor distribution statistics favored a non-centrosymmetric structure, the structure was successfully refined in the space group $I4/mmm$ (No. 139). Positions for the Gd and Cu atoms were based on the previous structure (Müller-Buschbaum & Wollschläger, 1975). The O atoms were located using difference Fourier methods; all atoms were refined *via* standard least-squares techniques. The scale factor, a secondary-extinction parameter (Zachariasen, 1967; Larson, 1967), atom coordinates and anisotropic temperature factors were ultimately refined. Neutral-atom scattering factors and appropriate anomalous-scattering terms were used (Cromer & Waber, 1974; Cromer, 1974). The final $R_f$ and $wR_f$ values are 2·8% and 3·7% with a goodness-of-fit parameter of 2·17 for the 102 reflections and 12 parameters. The ratio of the maximum least-squares shift to e.s.d. in the final refinement cycle is 5 × 10$^{-5}$. All calculations were performed on a CDC 7600 computer using an in-house package of programs. Atomic coordinates and anisotropic thermal parameters for $Gd_2CuO_4$ are listed in Tables 1 and 2.\*

**Discussion.** As previously noted (Grande, Müller-Buschbaum & Schweizer, 1977), the structure of Gd$_2$CuO$_4$ is not the distorted K$_2$NiF$_4$ type of La$_2$-CuO$_4$, but is of the type seen in Nd$_2$CuO$_4$ (Müller-Buschbaum & Wollschläger, 1975). An expanded view of Gd$_2$CuO$_4$ is depicted in Fig. 1. The Cu atoms, rather than being octahedrally coordinated by O atoms as in La$_2$CuO$_4$, exhibit a square-planar coordination. The framework of the Gd$_2$CuO$_4$ system consists of a two-dimensional edge-linked square-planar network of [CuO$_2$]$^{2-}$ groups which are linked by planes of Gd, O and Gd atoms. The Cu—O(2) distance in the square-planar array is 1·946 (1) Å; the Cu—O(1) and Cu—Gd distances are 3·550 (1) and 3·285 (1) Å, respectively. The Gd$^{3+}$ cation sites are eight coordinate rather than the nine-coordinate environment found for the larger La$^{3+}$ cation in La$_2$CuO$_4$ (Grande, Müller-Buschbaum & Schweizer, 1977). The O environment around each Gd$^{3+}$ is nearly cubic with a Gd—O(1) distance of 2·275 (1) Å and a Gd—O(2) distance of 2·646 (1) Å. The O(1)—O(2) distance is 2·969 (1) Å.

Possible lattice site vacancies for the atoms in Gd$_2$CuO$_4$ were probed by a least-squares refinement of site occupation factors for the Gd and the two O atoms. The site occupancy for the Cu atom was assumed to be 1·0 and was not refined. Anisotropic thermal parameters for all atoms and the $z$ fractional coordinate for the Gd were also refined. Convergence of the last least-squares refinement cycle resulted in a site occupancy of 0·99 (2) for the Gd, 1·04 (5) for O(1), and 0·98 (6) for O(2), indicating that the compound Gd$_2$CuO$_4$ is stoichiometric.

The $U_{11}$ thermal parameter for the O(2) atom in the Cu—O square-planar array is much larger than the anisotropic thermal parameters associated with the other atoms in the structure. The direction of thermal motion for this atom is in the Cu—O layer. The anisotropy of this particular O atom can be contrasted with that seen for the analogous O atom in the Cu—O layer in tetragonal La$_{1.85}$Sr$_{0.15}$CuO$_4$ (Wang *et al.*, 1987). In La$_{1.85}$Sr$_{0.15}$CuO$_4$, the thermal motion for the corresponding O atom is perpendicular to the Cu—O plane. The structure of La$_{1.85}$Sr$_{0.15}$CuO$_4$ has also been determined at 300, 60 and 10 K by neutron diffraction powder profile analysis (Cava, Santoro, Johnson & Rhodes, 1987). The structure is tetragonal at 300 K, but at *ca* 200 K undergoes a tetragonal-to-orthorhombic distortion. In La$_2$CuO$_4$, the orthorhombic distortion involves a puckering of the Cu—O planes through this O atom in the direction of the anisotropy, which Birgeneau *et al.* (1987) describe in terms of a low-lying optical mode which exhibits classical soft-mode behavior at the $X$ point (in *I*4/*mmm*) at $T_c = 425$ K. Our results suggest that, if second-order lattice instabilities are discovered in the Nd$_2$CuO$_4$ structural type, they will be of an entirely different nature than in La$_{1.85}$-Sr$_{0.15}$CuO$_4$.
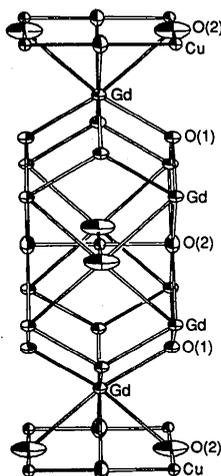
Fig. 1. Crystal structure of Gd$_2$CuO$_4$ showing the atomic numbering scheme. Symmetry-related atoms are labeled several times for the purposes of clarity. Thermal ellipsoids are at the 75% level.

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