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High-Pressure Behavior of LaNbO_4

BY J. W. E. MARIATHASAN*

Clarendon Laboratory, Parks Road, Oxford OX1 3PU, England

AND L. W. FINGER AND R. M. HAZEN

Geophysical Laboratory, Carnegie Institution of Washington, Washington DC 20008, USA

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Abstract

Unit-cell and crystal structure parameters of LaNbO_4 with a distorted scheelite structure have been refined at room pressure (489 reflections; weighted $R = 0.021$), at 1.55 GPa (207 reflections; weighted $R = 0.034$), and at 3.26 GPa (201 reflections; weighted $R = 0.034$). Compression is very anisotropic with maximum compressibility [$0.07(1) \text{ GPa}^{-1}$] near the (310) plane but expansion with increasing pressure [$-0.010(3) \text{ GPa}^{-1}$] approximately parallel to the [310] direction. The bulk modulus of LaNbO_4 (with $K' = 4$) is $0.111(3) \text{ TPa}$. The high-pressure structural behavior of LaNbO_4 , in which the monoclinic distortion increases with increasing pressure, is opposite to that of isostructural BiVO_4 . This behavior is related to structural instabilities that result in ferroelastic transitions in scheelite-type compounds. A value of $3.83 \text{ K}/0.1 \text{ GPa}$ is calculated for dT_c/dP . The high-pressure structure is analyzed in terms of bond-length-bond-strength concepts and the 'inverse' relationships of temperature and pressure.

Introduction

Ferroelastic properties of compounds with distorted scheelite structures, including BiVO_4 and the rare-earth niobates, have been of recent interest. Measurements of high-pressure Raman scattering, birefringence, and X-ray scattering have been made by

Pinczuk, Welber & Dacol (1979), Wood, Welber, David & Glazer (1980), and Hazen & Mariathasan (1982), respectively. The present study reports the high-pressure behavior of LaNbO_4 , which has a ferroelastic transition at high temperature similar to that of BiVO_4 . Lattice constants and structural parameters have been determined at pressures up to 3.26 GPa, and the variation of the transformation temperature with pressure has been estimated.

Understanding of the structure of rare-earth niobates has been confused since Barth (1926) first examined the mineral fergusonite, $\text{Y}(\text{Nb}, \text{Ta})\text{O}_4$, and concluded that it was tetragonal, isostructural with scheelite. Ferguson (1957) found that synthetic crystals of YTao_4 were monoclinic rather than tetragonal. This discrepancy was resolved by Komkov (1959), who showed that naturally occurring fergusonite could be transformed from a (metastable) scheelite structure to a stable monoclinic form by annealing. Komkov used Patterson syntheses to conclude that the space group must be $I2 (C_2^3)$ rather than $I2/a (C_{2h}^6)$ or $Ia (C_5^4)$, even though all three satisfy the systematic absences. Brixner, Whitney, Zumsteg & Jones (1977) used a Czochralski-pulled crystal to examine the domain structure of LaNbO_4 , observed only two types of domain walls, and concluded that the correct low-temperature space group had half the number of symmetry elements of the high-temperature group, $I4_1/a (C_{4h}^6)$. This conclusion implied a low-temperature symmetry of $I2/a (C_{2h}^6)$.

Although the three possible space groups have identical systematic absences, they belong to different point groups and have different symmetry in conver-

* Present address: Smith Associates, 45-47 High Street, Cobham, Surrey KT11 3DP, England.

gent-beam electron diffraction patterns. Tanaka, Saito & Watanabe (1980) used this technique to confirm that the space group is $I2/a$ (C_{2h}^6) and proved that the rare-earth niobates and tantalates with the monoclinic distorted scheelite structure are pure ferroelastics corresponding to the ferroic species $4/mF2/m$ in the terminology of Aizu (1969).

Experimental

Samples of LaNbO₄ from a Czochralski-pulled boule produced by the Clarendon Laboratory Crystal Growing Unit were cut in the form of (001) plates and polished to a thickness of 40 μm . The monoclinic setting with z unique is used in the study. Two separate fragments were selected. One, about $40 \times 40 \times 40 \mu\text{m}$, was used in the atmospheric-pressure study and was mounted in the normal fashion on a four-circle diffractometer. A second single-domain fragment, roughly $70 \times 70 \times 40 \mu\text{m}$ cut from the original sample, was mounted in a diamond-anvil cell with ruby chips for pressure calibration and a 4:1 methanol:ethanol pressure fluid. Each LaNbO₄ crystal was aligned with surfaces perpendicular or parallel to the incident X-ray beam to facilitate making absorption corrections. The lattice parameters (Table 1) were determined from the angles for 15 centered reflections, corrected for errors in crystal centering and diffractometer alignment by the method of Hamilton (1974) as modified by King & Finger (1979). Details of high-pressure crystal mounts and modifications to normal diffraction operations are given by Finger & King (1978) and Hazen & Finger (1982). Intensity data were measured with Nb-filtered, Mo radiation and θ - 2θ scans. The scan speed and background counting time were adjusted to yield a value of 0.01 for σ_I/I . All accessible reflections to $60^\circ 2\theta$ were measured, the intensities were corrected for absorption and Lorentz-polarization effects, and the symmetrically equivalent peaks were averaged to yield the structure-factor sets used in refinement. Observed variations in reference reflections indicated an underestimation of the structure-factor standard deviations, which were modified by $\sigma'^2 = \sigma^2 + (0.015F)^2$, where σ' is the 'corrected' standard deviation, σ is the standard deviation from counting statistics and F is the observed structure factor.

The initial high-pressure data set was collected at 3.26 GPa. After completion of these experiments, the pressure was lowered to 1.55 GPa, and intensities and lattice constants were remeasured. The pressure was then raised to 5.71 GPa; however, the surface of the crystal was observed to be covered by fine striations, intensities were greatly reduced, and it was impossible to obtain accurate unit-cell parameters. Preliminary unit-cell results were compatible with extrapolations from lower pressure. It is believed, therefore, that these changes in the crystal are not the result of a

Table 1. Crystallographic data and experimental conditions for LaNbO₄

	Standard temperature and pressure	1.55 GPa	3.26 GPa
a (\AA)	5.5634 (3)	5.5626 (6)	5.5528 (4)
b (\AA)	5.2030 (2)	5.1756 (7)	5.1456 (4)
c (\AA)	11.5227 (7)	11.451 (3)	11.365 (2)
γ ($^\circ$)	85.917 (4)	85.54 (1)	85.204 (6)
V (\AA^3)	332.81 (3)	328.66 (10)	323.59 (7)
Space group	$I2/a$	$I2/a$	$I2/a$
Z	4	4	4
D_x (g cm^{-3})	5.903	5.977	6.071
μ (Mo $K\alpha$) (cm^{-1})	158.6	160.6	163.1
Crystal size (mm)	$0.04 \times 0.04 \times 0.04$	$0.07 \times 0.07 \times 0.04$	$0.07 \times 0.07 \times 0.04$
Maximum 2θ ($^\circ$)	60	60	60
Number of symmetry-independent reflections	489	207	201
Number of reflections with $I > 2\sigma_I$	433	174	169
Weighted R	0.021	0.034	0.034
Conventional R	0.029	0.049	0.052

phase change at high pressure but are a consequence of nonhydrostatic effects arising from the crystal bridging the diamond anvils.

Refinement of the structural parameters was accomplished with program *RFINE4* (Finger & Prince, 1975). Starting parameters were derived from the neutron data of David (1981), weights were derived from the modified standard deviations, and the robust-resistant refinement scheme of Prince (1982) was used. Refined parameters included anisotropic thermal parameters and an isotropic-extinction coefficient. The atmospheric-pressure data set converged to parameters that are similar to those of David (1981) and Tsunekawa & Takei (1978), although the temperature factors obtained here are slightly smaller than previously determined. Refinements of the high-pressure data sets resulted in coordinates with standard deviations somewhat larger than for the ambient set, because of the reduced number of observations. The temperature factors for the high-pressure experiment are larger owing to uncertainties in diamond-cell absorption and a possible shielding of the crystal at high angles. In addition, thermal ellipsoids for Nb at 1.55 and 3.26 GPa and for O(1) at 3.26 GPa are nonpositive definite.* Crystallographic data and experimental conditions are listed in Table 1 and structural parameters are given in Table 2.

Pressure variation of the structure

Compression of LaNbO₄ between room pressure and 3.26 GPa is very anisotropic. The lattice actually expands with increasing pressure [$\beta_{\text{min}} = -0.010(3) \text{ GPa}^{-1}$] in the ab plane approximately

* Lists of structure factors and refined anisotropic temperature parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39851 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Structural parameters for LaNbO₄ at various pressures*

$$B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

Atmospheric pressure	x^*	y	z	B_{eq} (Å ²)
La	0	$\frac{1}{4}$	0.62935 (4)	0.45 (1)
Nb	0	$\frac{1}{4}$	0.10407 (6)	0.44 (1)
O(1)	0.7631 (6)	0.0526 (7)	0.0335 (3)	0.78 (6)
O(2)	0.8524 (6)	0.4882 (6)	0.2042 (3)	0.66 (7)
1.55 GPa				
La	0	$\frac{1}{4}$	0.6293 (3)	0.73 (10)
Nb	0	$\frac{1}{4}$	0.1029 (4)	0.44 (16)†
O(1)	0.7652 (17)	0.0501 (20)	0.0316 (26)	1.66 (68)
O(2)	0.8556 (22)	0.4877 (19)	0.2057 (20)	1.96 (84)
3.26 GPa				
La	0	$\frac{1}{4}$	0.6298 (3)	1.02 (12)
Nb	0	$\frac{1}{4}$	0.1009 (4)	0.33 (17)†
O(1)	0.7687 (19)	0.0421 (19)	0.0320 (25)	0.06 (77)†
O(2)	0.8483 (22)	0.4844 (19)	0.2086 (21)	1.89 (82)

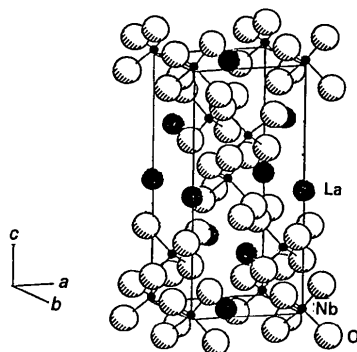
* Coordinates are given relative to an origin at a center of inversion, which is located at $0, \frac{1}{4}, \frac{1}{8}$ from the choice of David (1981).

† Anisotropic ellipsoids are nonpositive-definite because β_{33} is slightly negative.

along [310]. Maximum compression is found perpendicular to this direction in the (310) plane [$\beta_{\text{max}} = 0.07(1) \text{ GPa}^{-1}$]. The bulk modulus of LaNbO₄, calculated with a first-order, Birch–Murnaghan equation of state from pressure–volume data, is 0.111(3) TPa.

A representation of the structure of LaNbO₄ is shown in Fig. 1, and the bond distances for the cation–anion polyhedra are listed in Table 3. The La³⁺ ion is surrounded by eight O atoms at distances from 2.48 to 2.55 Å under room conditions. The Nb⁵⁺ ion is surrounded by four O atoms at 1.84 to 1.91 Å and two at 2.54 Å. The eight-coordinated La polyhedron undergoes significant compression between room pressure and 3.26 GPa, whereas the Nb polyhedron is relatively incompressible over the same pressure range.

Bond lengths and corresponding bond strengths (Brown, 1973; Brown & Wu, 1976) for the O polyhedra surrounding the La³⁺ and Nb⁵⁺ ions are listed in Table 4. Although the errors in the bond lengths at high pressure are large, the Nb coordination (Fig.

Fig. 1. A perspective view of the structure of LaNbO₄.Table 3. *Bond lengths and strengths for LaNbO₄ at various pressures*

	Bond length (Å)			Bond strength		
	0 Pa	1.55 GPa	3.26 GPa	0 Pa	1.55 GPa	3.26 GPa
La–O(1) (2×)	2.484 (3)	2.489 (15)	2.469 (14)	0.412	0.406 (15)	0.429 (16)
La–O(2) (2×)	2.463 (3)	2.469 (14)	2.443 (14)	0.435	0.428 (15)	0.461 (17)
La–O(1') (2×)	2.550 (3)	2.529 (22)	2.547 (22)	0.347	0.367 (20)	0.347 (17)
La–O(2') (2×)	2.523 (3)	2.495 (18)	2.482 (18)	0.372	0.400 (20)	0.414 (19)
Mean of 8	2.505	2.50	2.49			
Σ s				1.566	1.60 (7)	1.65 (7)
Nb–O(1) (2×)	1.910 (3)	1.911 (17)	1.907 (17)	0.992	0.99 (4)	1.01 (4)
Nb–O(2) (2×)	1.843 (3)	1.840 (17)	1.869 (18)	1.186	1.19 (5)	1.12 (5)
Nb–O(1') (2×)	2.536 (3)	2.483 (20)	2.422 (19)	0.240	0.27 (1)	0.30 (1)
Mean of 4	1.876	1.88	1.89			
Σ s				2.418	2.45	2.43
Mean of 6	2.096	2.08	2.07			

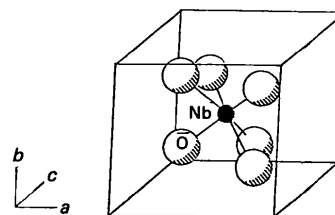
Table 4. *Spontaneous strain components in monoclinic LaNbO₄ at various pressures*

Strain component	0.1 MPa	1.55 GPa	3.26 GPa
ϵ_{11}^2	0.03710 (1)	0.03611 (1)	0.03815 (1)
ϵ_{12}^2	0.03565 (4)	0.03898 (8)	0.04188 (6)
ϵ^3	0.06939 (5)	0.0751 (1)	0.0801 (1)

2) seems to be approaching an octahedron, as expected at high pressure (David, 1981). In particular, the Nb–O(1') distance decreases by 5.6 standard errors between atmospheric pressure and 3.26 GPa, whereas Nb–O(1) and Nb–O(2) are reduced by insignificant amounts, 0.3 and 1.4 standard errors, respectively. These effects weaken the 'short-range' forces and strengthen the 'long-range' values. The strengths of the weak Nb–O(1') bonds increase, with a possible decrease in the strengths of the strong Nb–O(1) and Nb–O(2) bonds.

Variation of transition temperature with pressure

As pressure is increased, both $a-b$ and $\pi/2-\gamma$ increase (Table 1). These increases imply an increase in transition temperature as well as ferroelastic distortion with increasing pressure. This result contradicts Samara (1977), who used the soft-mode theory of Cochran (1960) to conclude that increasing pressure should decrease the temperature of a ferrodistortive transition owing to the decrease in interatomic distances. David (1981) used Ehrenfest's equation with

Fig. 2. Details of the distorted O octahedron around Nb in LaNbO₄.

a Landau expansion of the free energy to show that near the phase transition

$$dT_c/dP = k(\alpha_b - \alpha_a), \quad (1)$$

where α_a and α_b are the temperature coefficients of volume expansion just above and below the transition, respectively, and k is a positive constant of proportionality. The transition temperature, therefore, will increase if the thermal expansivity of the high-temperature phase is greater than that of the low-temperature form.

From neutron powder-profile refinements of LaNbO₄ at a number of temperatures, David (1981) observed that the monoclinic unit-cell volume was less than that of the extrapolated high-temperature tetragonal form. This observation implies an increase in transition temperature with increasing pressure, a result opposite to that for BiVO₄. David postulated that Samara's arguments for the rare-earth, fergusonite-type structures were incorrect because of induced changes in the coordination of the Nb⁵⁺ ion from tetrahedral to octahedral, which effectively increase the nearest-neighbor distances. This trend toward increased coordination number of Nb is reflected in bond-distance data (Table 3).

The spontaneous strain components for monoclinic symmetry from infinitesimal strain theory are given by

$$\varepsilon_{11}^s = (a - b)/[2(ab \sin \gamma)^{1/2}], \quad (2)$$

$$\varepsilon_{12}^s = \tan[(\pi/2 - \gamma)/2], \quad (3)$$

and

$$(\varepsilon^s)^2 = 2[(\varepsilon_{11}^s)^2 + (\varepsilon_{12}^s)^2]. \quad (4)$$

Table 4 lists the values for these strain components in LaNbO₄ at the pressures studied. The magnitudes are large, with ε^s approximately 7% under ambient conditions and increasing to 8% at 3.26 GPa. The temperature dependence of the spontaneous strain in LaNbO₄ has been fitted (David, 1981) to the function

$$(\varepsilon)^2 = A(T_0 - B \coth B/T), \quad (5)$$

which yields the transition temperature by setting the strain to zero at T_c . David (1981) obtained values for the variable parameters from which an estimate of 766 K for T_c was made, in agreement with the measured value of 768(3) K (Takei & Tsunekawa, 1977). At atmospheric pressure, $(\varepsilon^s)^2$ is 4.81×10^{-3} . Application of pressure increases this quantity to 5.65×10^{-3} at 1.55 GPa and to 6.42×10^{-3} at 3.26 GPa.

The magnitude of the variation of transition temperature with pressure can be estimated from assumptions about the variation with pressure of A , B and T_0 in equation (5). These constants are given by

$$\begin{aligned} A &= 3sk/\omega^2 \\ B &= h\omega/2K \end{aligned} \quad (6)$$

$$T_0 = \{[\nu(0) - 2a_1]/4a_2\}\omega^2/3K,$$

where ω is a single, temperature-independent effective frequency, $\nu(0)$ describes the interaction potential between a local oscillator and the remainder of the crystal, a_1 and a_2 are the coefficients of a displacement variable (ξ) in the expression for the local potential,

$$V(\xi) = a_1\xi^2 + a_2\xi^4,$$

and s is a scale factor relating ξ to the spontaneous strain (David, 1981; David & Wood, 1983).

Hydrostatic pressure should not change s , the scaling factor, which is assumed to be a constant, characteristic of the material. As there is no high-pressure transition, none of the frequencies of the vibrational modes of the crystal becomes soft at high pressure; therefore, it is reasonable to assume that the effective frequency, ω , is essentially constant with pressure. Changes in transition temperature with pressure are a result of variations in T_0 . Values of this parameter can be estimated from the experimental values of $(\varepsilon^s)^2$ and the values of A and B obtained by David (1981). This procedure yields T_0 equal to 924 K at 1.55 GPa and 978 K at 3.26 GPa. Values of T_c are 831 K at 1.55 GPa and 891 K at 3.26 GPa. These values correspond to a linear dependence of the transition temperature on pressure with dT_c/dP equal to 3.83 K/0.1 GPa. A combined high-pressure-high-temperature birefringence study of LaNbO₄ with the technique described by Wood, Welber, David & Glazer (1980) could verify this result.

Inverse relationship between temperature and pressure

In many materials, structural changes on cooling from high temperature are similar to those on compression; this behavior is qualitatively true for LaNbO₄. The inverse relationship is generally true when (i) all polyhedra in a structure have similar ratios of expansivity to compressibility, or (ii) one polyhedron is relatively rigid compared with the rest of the structure. These conditions are fulfilled by all materials that have only one type of cation polyhedron and a great many silicates that have only one type of polyhedron other than the relatively rigid Si tetrahedron. Conformity with this inverse relationship can be demonstrated by plotting structural parameters against the relative volume V/V_0 (Hazen & Finger, 1982). Fig. 3 shows a , b , c and γ of LaNbO₄ in such a plot, which includes the high-temperature data of David (1981) and the high-pressure data of this study. Fig. 4 shows the fractional coordinates of the La and Nb cations plotted against relative volume. If pressure and temperature were exactly analogous, the variation of unit-cell and positional parameters would be linear *versus* relative volume. It is evident from Figs. 3 and 4 that although the effects of pressure and temperature are similar, the structural parameters are not dependent only on molar volume, *i.e.* the com-

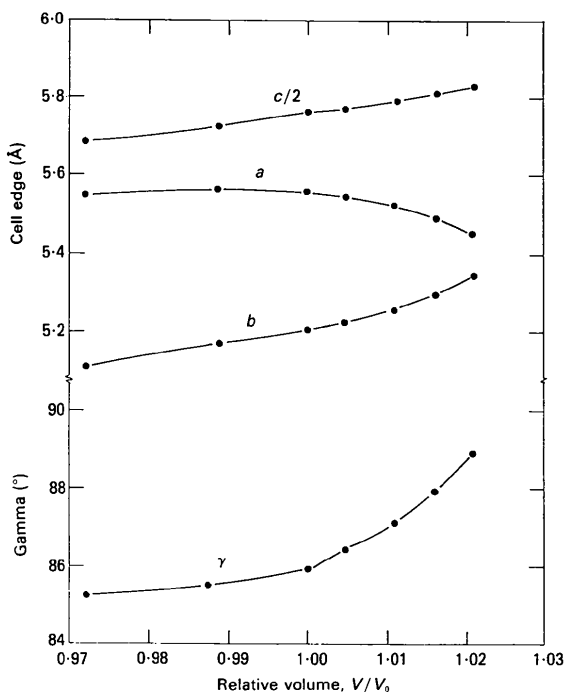


Fig. 3. Variation of LaNbO_4 unit-cell parameters, measured at several temperatures and pressures, versus relative volume (V/V_0). Lines connect observed values and do not represent calculated curves.

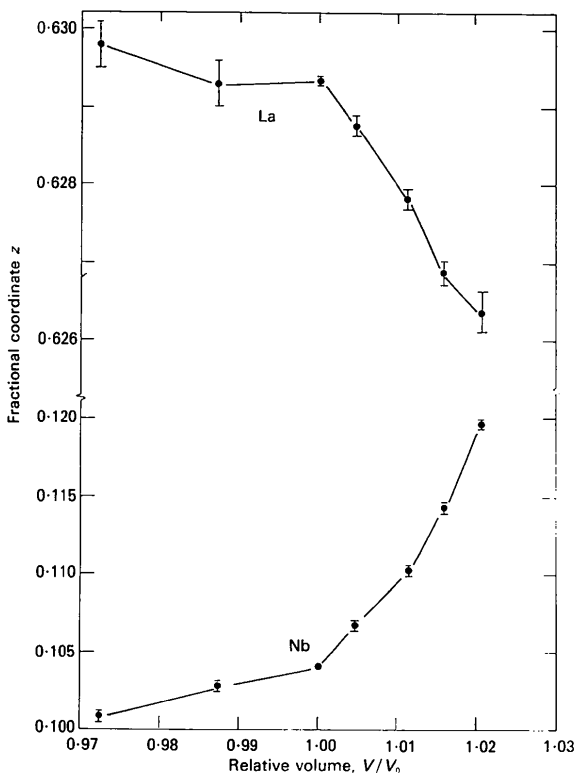


Fig. 4. Variation of atomic coordinates of La and Nb, measured at several temperatures and pressures, versus relative volume (V/V_0). Lines connect observed values and do not represent calculated curves.

ponent polyhedra do not satisfy the requirements for an inverse relationship. The fractional coordinates of the La^{3+} and Nb^{5+} ions are nearly invariant with compression, but vary significantly with thermal expansion. The same result is found for all lattice constants except for the c axis, which is linear in V/V_0 . This result occurs because the spontaneous strain in the ferroelastic phase is dependent only on the cell parameters in the plane perpendicular to the c axis [equations (2) and (3)]; i.e. a , b and γ .

The differences between high-temperature and high-pressure induced changes in the structural parameters could be explained by the high-temperature phase transition. The structure is unstable in the temperature range measured, and temperature changes have produced anomalously large differences in the structural parameters, caused by softening of, in this case, an acoustic mode of vibration. High-pressure changes, however, do not produce a phase transition, and the structure shows a normal response to pressure. If the structural parameters were obtained at very low temperature, where the ferroelastic distortions were saturated, it is predicted that the parameters would show a similar variation versus relative cell volume for both temperature and pressure changes. Hazen & Finger's (1982) conclusions about the inverse relationship of pressure and temperature are, therefore, subject to the requirement that the structure is not in the vicinity of a phase transition, which would produce an anomalously large variation in the variable producing the transition.

One can extend this analysis and speculate on a method by which the existence of high-pressure or high-temperature phase transitions in new materials may be predicted. If the structural parameters as a function of relative cell volume are plotted over the temperature and pressure range available, and if the parameters do not lie on a smooth curve, phase transitions are likely to occur at temperatures and pressures close to those at which the anomalies are observed.

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Electron Density in Non-Ideal Metal Complexes. I. Copper Sulphate Pentahydrate

BY J. N. VARGHESE AND E. N. MASLEN*

Crystallography Centre, University of Western Australia, Nedlands, Western Australia 6009, Australia

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Abstract

The structure of copper sulphate pentahydrate was refined using an accurate set of X-ray data: $M_r = 249.68$, triclinic, $P\bar{1}$, $a = 6.1224$ (4), $b = 10.7223$ (4), $c = 5.9681$ (4) Å, $\alpha = 82.35$ (2), $\beta = 107.33$ (2), $\gamma = 102.60$ (4)°, $V = 364.02$ (3) Å³, $Z = 2$, $D_x = 2.278$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 3.419$ mm⁻¹, $F(000) = 254.0$, $T = 298$ K, $R = 0.039$ for 7667 reflections. The structural parameters are compared with those obtained by neutron diffraction. The differences between X-ray and neutron positions are related to the hydrogen bonding in the structure. The dominant features in the residual density near the two crystallographically independent Cu atoms result from the redistribution of $3d$ electrons due to bonding. The density is anisotropic, as expected in view of the Jahn-Teller distortion in the structure. Marked differences in the d -electron distributions for the two Cu atoms correlate with small variations in molecular geometry. Second-nearest-neighbour effects, such as those arising from differently oriented ligating waters, are significant in this structure. Sharp features in the difference density close to the Cu nuclei are similar to those in other Cu²⁺ complexes, indicating that the electron density in this region is more reliable than previously believed.

Introduction

Diffraction methods for the study of electron density in crystalline materials comprising first-row atoms are

now well established. Charge density analyses for crystals containing heavier atoms are more difficult, in general, since the valence scattering is a lower fraction of the total for the structure. Paradoxically the case of d electrons for the heavier members of the first transition series of elements is rather favourable. Their distributions are contracted, in comparison with those for the lighter members. Because the scattering for these electrons extends correspondingly further in reciprocal space, they can be studied more accurately.

Iwata & Saito (1973) exploited this in pioneering work on hexaamminecobalt(III) hexacyanocobaltate(III). In subsequent analyses of transition-metal complexes with near-to-ideal geometry, concordance between the charge density maps and the predicted d -electron orbital occupancies was established. Lighter members of the first transition series were studied successfully by averaging regions of the electron density which, although crystallographically independent, are chemically equivalent (Rees & Mitschler, 1976). This included cases where the d electrons are involved directly in covalent bonding (Toriumi & Saito, 1978).

Qualitative information on the bonding electron distribution has already proved to be helpful in systems with non-ideal geometries, such as metal-metal bonds, where the bonding mechanism was not well understood (Wang & Coppens, 1976; Mitschler, Rees & Lehmann, 1978). In most cases, however, the nature of the stronger forces affecting the electron density distribution is well known. If charge density studies are to make a useful contribution to knowledge they

* Author to whom correspondence should be addressed.