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GEOMETRICAL AND ELECTROSTATIC COMPARISON OF THE CuO STRUCTURE TYPE WITH THE PtS and NaCl STRUCTURE TYPES*

J. ZEMANN

Institut fuer Mineralogie und Kristallographie, Universitaet Wien, Dr. Karl Lueger-Ring 1, A-1010 Wien, Austria

ABSTRACT

Geometry shows that the CuO structure type can be described not only as a distorted PtS type, but also as a distorted NaCl type. Madelung constants computed for a number of models of the three structure types indicate that: (1) radially symmetric forces alone cannot explain the stereochemistry of CuO; (2) consideration of the Jahn-Teller effect is probably not a sufficient extension of the theory; as a consequence, (3) directed covalent bonds seem to play an important role in stabilizing the atomic arrangement.

SOMMAIRE

On montre géométriquement que le type structural CuO représente une distortion, non seulement du type PtS, mais aussi du type NaCl. Les valeurs de la constante de Madelung calculées pour plusieurs modèles des trois types structuraux indiquent que 1) les forces radiales symétriques à elles seules ne suffisent pas à expliquer le stéréochimie de CuO, 2) l'effet Jahn-Teller ne fournit probablement pas une extension suffisante de la théorie et, par conséquent, (3) les liaisons covalentes directionnelles semblent jouer un rôle important dans la stabilisation de l'agencement des atomes.

(Traduit par la Rédaction)

INTRODUCTION

The atomic arrangement of tenorite, CuO, is unique among all compounds of formula type *AB*. According to the original structure determination by Tunell *et al.* (1935) and to the refinement by Åsbrink & Norrby (1970) the space group is $C2/c - C_{2h}^6$; four Cu atoms occupy the position (4*c*) ¼ ¼ 0, *etc.* (point symmetry: $\bar{1}$) and four O atoms occupy the position (4*e*) 0 *y* ¼, *etc.* (point symmetry: 2) with $y \sim 0.42$. The structure is characterized by a planar rectangular coordination of four oxygens around copper at almost equal distances with two more oxygens approximately 42% farther away to complete a strongly distorted octahedral coordination. The shortest Cu–Cu distances are ~ 15% longer than in metallic copper. Oxygen is surrounded by four copper atoms in the form of a strongly distorted tetrahedron.

The crystal-structure refinement (Åsbrink & Norrby 1970) has resulted in Cu–O bond lengths $d_1 = 1.9509(26)$, $d_2 = 1.9608(13)$ and $d_3 = 2.7840(37)$ Å (each 2×) and a CuO_4 rectangle 2.6246(19) by 2.9005(3) Å. The deviation of the long Cu–O bond d_3 from the normal at the CuO_4 rectangle is 17°. The Cu–O–Cu angles in the CuO_4 tetrahedron were found to vary from 95.72(4) to 145.82(25)°.

The CuO structure type can be described as a monoclinic distorted PtS type (Bannister 1932, Grønvold *et al.* 1960), an oxygen-bearing representative of which is PdO (Waser *et al.* 1953). This relation is common knowledge in crystal chemistry (*e.g.*, Wells 1975). The CuO structure type can, however, also be described as a monoclinic distorted NaCl type. This has, to the best of the author's knowledge, not been reported in the literature as yet.

GEOMETRIC RELATIONS BETWEEN THE CuO, PtS AND NaCl STRUCTURE TYPES

To illustrate these geometric relations Figure 1 gives the [010] projections of the CuO, PtS and NaCl structure types for the chosen monoclinic cell. The numerical values of the crystallographic constants are listed in Table 1. Data in this table pertain not only to the structure of CuO as determined by Åsbrink & Norrby (1970) but also to two idealized models in which the *A–B* distances in the AB_4 rectangle are made exactly equal. These idealizations cause only minor changes in the atomic arrangement compared with the observed structure, in which the two kinds of short *A–B* distances differ in length by 0.5% only.

If kept tetragonal, the PtS structure type, normalized to *A–B* = 1 in the AB_4 rectangle, has one degree of freedom. The angle ω be-

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*Dedicated to Professor J. D. H. Donnay on the occasion of his 75th birthday.

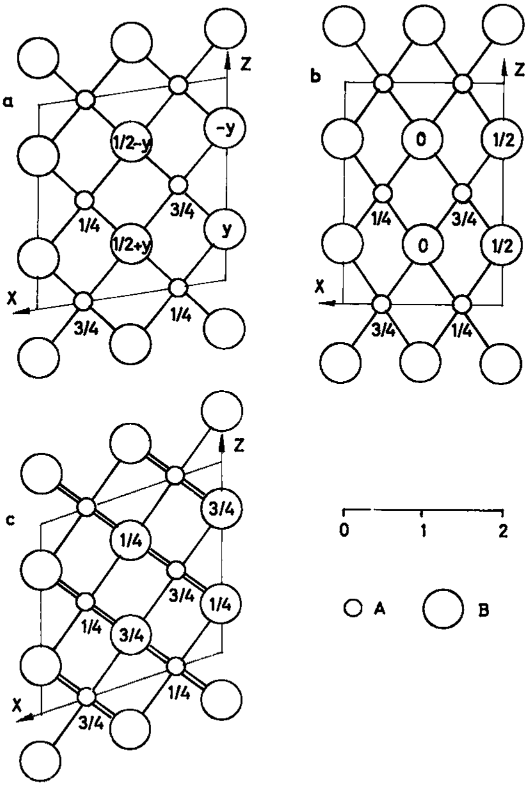

FIG. 1. The atomic arrangement of (a) the CuO structure type, (b) the PtS structure type and (c) the NaCl structure type projected parallel to [010] of the chosen monoclinic cell (space group: $C2/c$ –C_{2h}^{6}). The numerical values of the crystallographic constant are listed in Table 1.

tween any of the A–B bonds and the direction [001] of the tetragonal cell (= [001] for the monoclinic cell of Table 1 also) is chosen as the variable ($0° < \omega < 90°$). Table 1 shows two "ideal" models, namely the one with geometrically ideal AB_4 squares ($\omega = 45°$, model I) and the one with geometrically ideal BA_4 tetrahedra ($\omega = \arctan\sqrt{2} \sim 54.74°$, model II). For both PtS and PdO (Bannister 1932, Grønvold *et al.* 1960, Waser *et al.* 1953) the experimentally determined structure has $\omega \sim 49°$. It should be noted that in all tetragonal PtS models the A atoms have a rather clear-cut planar 4-coordination of B atoms. Next-nearest neighbors (normalized to A–$B_{\min} = 1$) occur at 1.4142 and 1.6330 for PtS models I and II, respectively. Beyond these, *eight B* neighbors occur at equivalent crystallographic distances. The monoclinic distortion of the PtS to the CuO structure type causes two of these eight distances to become shorter than the rest.

For the NaCl structure type Table 1 gives the monoclinic description of the ideal cubic structure as well as that of two tetragonally distorted structures (models II and III) in which the AB_6 octahedra are elongate parallel to one of the fourfold axes; the four short A–B bonds measure 1.0000; the two long ones have the same values as the long A–B bonds in CuO models II and III, respectively. Whereas in both CuO and PtS structure types the AB_4 squares lie alternatively parallel to (110) and (1$\bar{1}$0), the AB_4 squares of NaCl models II and III all lie parallel to (10$\bar{1}$) of the chosen monoclinic cell. One can, of course, also describe these two models in a tetragonal cell with [001] in the direction of [10$\bar{1}$] of the monoclinic cell used here; the AB_4 squares then lie parallel to (001). Furthermore, it seems worth mentioning that in the CuO and PtS structure-type models the BA_4 coordination figures are tetrahedra, whereas in NaCl structural models II and III, they are undistorted squares.

CHEMICAL BONDING IN CuO

The arrangement of four coplanar ligands around Cu(II) is usually interpreted as a consequence of covalent bonding of copper (*cf.*, Pauling 1960). In cases where a clear (4 + 2) coordination around Cu(II) is observed, ionic bonding and Jahn-Teller distortion are commonly assumed to explain the stereochemistry (*e.g.*, Burns 1970). From the electronegativity difference between copper and oxygen Åsbrink & Norrby (1970) concluded that the bonding in CuO is probably mainly covalent. Wells (1975, p. 887) states that the chemical bond between Cu(II) and O is generally expected to have a considerable degree of ionic character. When dealing specifically with CuO, this author (1975, p. 896) is careful to say only in this connection that this oxide provides the simplest example of Cu(II) forming four coplanar bonds. Burns (1970, p. 109), however, clearly states that tenorite contains Cu^{2+} ions in sites distorted from regular octahedral symmetry by the Jahn-Teller effect. For the determination of the valence-band structure in tenorite by X-ray photoemission spectroscopy the reader is referred to Wertheim & Hüfner (1972).

In connection with the geometric consideration given above two questions pertaining to stereochemistry are of interest: (1) If the CuO bond in tenorite is essentially covalent, why does this compound not have the PdO structure? (2)

TABLE 1. GEOMETRIC DESCRIPTION IN SPACE GROUP $C2/c$ AND MADELUNG CONSTANT α OF SOME MODELS OF THE CuO, PtS AND NaCl STRUCTURE TYPES*

	CuO type			PtS type		NaCl type		
	I	II	III	I	II	I	II	III
a	2.3947	2.3947	2.3927	2.0000	2.3094	2.4495	3.1788	3.1680
b	1.7500	1.7499	1.7485	2.0000	2.3094	1.4142	1.4142	1.4142
c	2.6223	2.6211	2.6201	2.8284	2.3094	2.4495	3.1788	3.1680
β	99.54°	99.26	99.54	90.00	90.00	109.47	127.17	126.97
y	0.4184	0.4175	0.4150	0.5000	0.5000	0.2500	0.2500	0.2500
α	1.6290	1.6290	1.6296	1.6049	1.5802	1.7476	1.6358	1.6363

* The electropositive elements (A atoms) in position ($4c$): $\frac{1}{4}$ $\frac{1}{4}$ 0, *etc.*; the electronegative atoms (B atoms) in position ($4e$): 0 y $\frac{1}{4}$, *etc.*

CuO type, Model I: Structure as determined by Åsbrink & Norrby (1970), normalized to $(d_1+d_2)/2 = 1.0000$; α is also normalized to $(d_1+d_2)/2$. The Madelung constant of the actual CuO structure for the smallest A-B distance is 1.6248.

CuO type, Model II: This model is constructed so that, in comparison to the actual structure, the following requirements are fulfilled: 1) in the AB_4 rectangle, $d_1=d_2=1.0000$; 2) in the AB_4 rectangle, B-B(long)/B-B(short) = O-O(long)/O-O(short) in the actual CuO_4 rectangle; 3) A-B(long) = Cu-O (long)/$\bar{d}$ in the actual structure $[\bar{d}=(d_1+d_2)/2]$, *i.e.*, A-B(long) = 1.4234; 4) a/b = a/b in the actual structure.

CuO type, Model III: 1) $a{:}b{:}c$ and β as in actual structure; 2) parameter y shifted so that $d_1=d_2$; 3) $d_1=d_2=1.0000$; A-B(long) becomes 1.4174.

PtS type, Model I: 1) A-B = 1.0000; 2) geometrically ideal AB_4 squares (ω = arctan1 = 45°).

PtS type, Model II: 1) A-B = 1.0000; 2) geometrically ideal BA_4 tetrahedra ($\omega = \arctan\sqrt{2}$ = 54.74°).

NaCl type, Model I: ideal cubic NaCl type with A-B = 1.0000.

NaCl type, Model II: NaCl type distorted parallel to one of the fourfold axes so that A-B(short) = 1.0000 (4x) and A-B(long) = 1.4234 (corresponding to the A-B distance d_3 in AB_6 'octahedron' of CuO model II).

NaCl type, Model III: NaCl type distorted parallel to one of the fourfold axes so that A-B(short) = 1.0000 (4x) and A-B(long) = 1.4174 (2x) corresponding to the A-B distance d_3 in AB_6 'octahedron' of CuO model III.

If the bonding in tenorite is mainly ionic with Jahn-Teller distortion in the coordination polyhedron around copper, why does it not crystallize with the NaCl structure and Jahn-Teller distortion parallel to one of the fourfold axes? The last question has also been asked by Wells (1975, p. 890). He tentatively suggests that the lattice energy of such a structure would be smaller than that of tenorite, but unfortunately, results of calculations are not available.

COMPUTATION OF MADELUNG CONSTANTS AND DISCUSSION

As a contribution to an answer to these questions, Madelung constants α were computed for the structures listed in Table 1 and for some other geometrically closely related structures, using the program of R. Fischer in Fischer & Ludwiczek (1975) based on the formulas of Bertaut (1952). Except for CuO model I, the A atoms are surrounded by four B atoms to form a planar rectangular (or in some special cases planar square) AB_4 configuration with equal A–B distances. Two of the models, *i.e.*, CuO models II and III, are very good approximations of the experimentally determined structure. The ideal case of four exactly equal A–B distances in the AB_4 rectangle was chosen as it reduces the number of variables.

All the Madelung constants α given in this paper are normalized to one formula unit AB and, unless explicitly stated otherwise, to the smallest A–B distance. With this normalization, models with equal A–B distances in the AB_6 polyhedra show the maximum in α exactly for, or very close to, the model with maximum cell volume (O'Keefe 1977).

Important complements to Table 1 are Figures 2 and 3. Figure 2 gives the Madelung constant α of the (tetragonal) PtS type as a function of ω. The maximum value of α lies between the two geometrically "ideal" models, near the observed value of ω. Figure 3 shows for the tenorite type the variation in α for models in which the dimensions of the AB_4 rectangle and the length of d_3 are kept at the values of CuO model II. It should be borne in mind that the *orientation* of

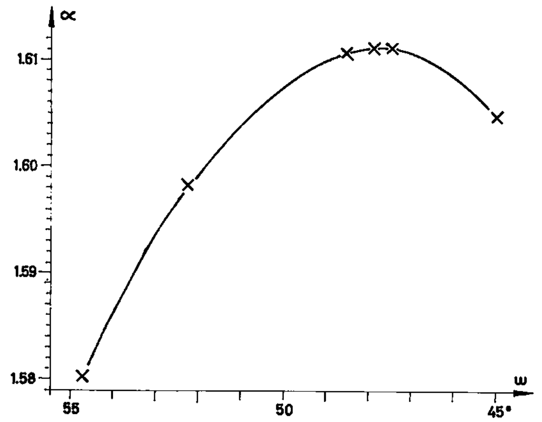

FIG. 2. Madelung constant α of the (tetragonal) PtS structure type as a function of ω, *i.e.*, the angle between the direction of any of the shortest A–B bonds with the Z axis ($0<\omega<90°$).

d_3 relative to the AB_4 rectangle is allowed to vary. Such models have only one degree of freedom, chosen arbitrarily to be lattice constant b.

The following results of the computations seem to be of interest in connection with the questions under consideration: (1) All Madelung constants α for the CuO structure type given in Table 1 and Figure 3 exceed that for any tetragonal PtS type structure (Table 1, Fig. 2). Therefore, a deformation of the PtS structure type towards the CuO structure type *can* be interpreted as a consequence of the electrostatic part of the lattice energy. (2) All Madelung constants α of representatives of the CuO structure type given in Table 1 and Figure 3 are considerably smaller than that of the ideal (cubic) NaCl type, into which the tenorite type can be deformed without crossing geometric barriers (*cf.*, Fig. 1a and c). (3) Compared with the values for CuO models II and III, the Madelung constants of the tetragonally deformed NaCl type with the same distances d_3 are larger by $\sim$ 0.4% (Table 1). This result does not support the assumption that it is possible to explain the stability of the tenorite structure by an ionic model wih the only further consideration being Jahn-Teller distortion. (4) Keeping all dimensions of the AB_4 rectangle as well as the length of d_3 constant, CuO model II (and evidently other similar models also) can be deformed into an electrostatically very slightly ($\sim$ 0.1%) more favorable geometry (Fig. 3). However, the Madelung constant α remains smaller than that of the tetragonally deformed NaCl type with the same d_3. The difference in electrostatic lattice energy between CuO model II and this electrostatic optimum is only $\sim$1 kcal/mole even for a fully ionic model (with Cu–O $\sim$ 2 Å). No explanation for this small effect will be attempted here.

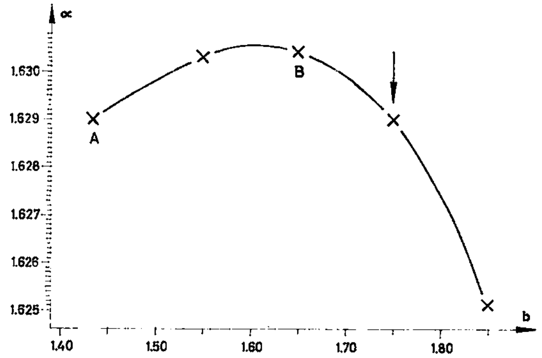

FIG. 3. Madelung constant α of CuO models fulfilling the conditions (1) to (3) of CuO type model II of Table 1, as a function of the lattice constant b. The model marked with an arrow corresponds to CuO model II. Model A corresponds to an orthorhombically deformed PtS type with a 2.5971, b 1.4326, c 2.6838 and $\alpha = \beta = \gamma = 90°$, model B (near the maximum of α) to a CuO type structure with a 2.4647, b 1.6500, c 2.6529, $\alpha = \gamma = 90°$, $\beta = 95.883°$ and $y = 0.4385$.

The results of the computations as summarized above are in agreement with the common view that radially symmetrical forces alone cannot explain the geometry of tenorite, nor of Cu(II) in general. These computations indicate that consideration of the Jahn-Teller effect is probably not sufficient as the only modification of the theory, and support the view that directed covalent forces with a tendency to form a tetrahedral coordination around oxygen and a plane square around copper play an important role in the stabilization of the geometry of tenorite.

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