

Structural units of cuprates in natural Cu-oxysalts

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The structure of copper oxysalt minerals is analyzed on the basis of the classification scheme developed earlier for synthetic cuprates. The copper–oxygen compounds were considered as the salts of hypothetical copper acids with characteristic Cu-containing structural units of various dimensions formed by a polymerization of the CuO squares. The results of magnetic susceptibility measurements performed recently were analyzed from the viewpoint of the developed extended structural classification scheme. The dimerization of magnetic moments was considered as a property of cuprates which was strongly dependent on the type of Cu-containing structural unit. A further extension of the structural classification scheme for cuprates is also discussed.

1. Introduction

Until the discovery of high- T_c superconductivity, copper–oxygen compounds were traditionally considered as copper salts of various inorganic acids or as complex oxides. This was justified by the fact that, in numerous synthetic compounds and minerals, the role of Cu atoms was similar to that of Fe, Mg, Ti, Sn *etc.*, and that Cu was five- or sixfold coordinated by O atoms.

After the discovery of high- T_c superconductivity in 1986, new series of copper–oxygen compounds were widely investigated, in which Cu was fourfold coordinated by O atoms and assigned to particular Cu–O structural complexes. The important role of CuO₂ planes and CuO₂ chains was understood in such phenomena as high- T_c superconductivity and magnetic effects due to ordering of magnetic moments. In a search of new superconductors, numerous copper–oxygen compounds were synthesized, the structures of which were based on the Cu-containing motives composed of variously polymerized CuO squares. In this respect, a structural similarity of copper–oxygen compounds with well investigated silicates and borates allowed the separation of the individual class of cuprates (Leonyuk *et al.*, 1997), as the salts of hypothetical copper acids. The structural classification scheme for cuprates was developed (Leonyuk *et al.*, 1998). Therefore, the fourfold coordination of Cu atoms is assumed to indicate the role of copper as acid-forming element by analogy with Si, B *etc.*

The similarity of the structural units for acid complexes in cuprates and silicates should also be noted: the side and diagonal of the CuO square are equal to the edge of the SiO₄ tetrahedron and to the edge of the diortho group Si₂O₇, respectively. As is known (Belov, 1976), separate SiO₄ tetra-

hedra are found in Fe and Mg silicates while the diortho group Si₂O₇ is characteristic of silicates with larger cations like Ca. The structural similarity mentioned above indicates a possible existence of a large variety of cuprates.

In searches for new magnetic Cu-containing compounds, it was noticed that there is a large group of so-called Cu-containing natural oxysalts, in which only a part of the O atoms belongs to various acid radicals. On the one hand, regarding this feature, Cu-containing oxysalts were assigned as carbonates, sulfates, arsenates, vanadates *etc.* On the other hand, if Cu is fourfold coordinated in such a structure and the polymerized CuO squares form a certain motif characteristic of cuprates, then the compound can also be described as a cuprate. If all O atoms are prescribed to acid motives, such a compound formally cannot be determined as an 'oxysalt'. As a result, a part of the 'oxysalts' is assigned to the group of 'double salts', in which the physical properties owing to the presence of the Cu–O motif characteristic of cuprates can be observed.

The classification scheme regarding the structural units can be used to reveal the general regularities in the structure of copper–oxygen compounds. Several aspects of such a classification should be emphasized.

(i) The extension of the group of cuprates would be important for analysis of cuprates as an individual class of inorganic compounds.

(ii) All cuprates considered in the previous classification scheme (Leonyuk *et al.*, 1998) were grown from the melt, while oxysalts, both natural and synthetic, were usually formed under a hydrothermal process. Therefore, a separation of cuprates among oxysalts would allow one to reveal the dependence of particular structural features on the type of crystallization.

(iii) The presence of characteristic acid radicals allows one to assume a possible manifestation of related physical properties in various compounds. Owing to the magnetic moment of the Cu^{2+} ion, Cu-containing oxysalts can be considered as compounds that are prospective for the studies of magnetic properties and for a search of new magnetic materials.

In the present work, the structures of copper oxysalt minerals are analyzed and classified on the basis of the previous classification scheme for cuprates (Leonyuk *et al.*, 1998). The results of magnetic susceptibility measurements performed recently (Maltsev *et al.*, 2001) were analyzed from the viewpoint of the developed extended structural classification scheme. Finally, a further extension of the classification scheme is discussed for revealing the general structural regularities in mixed salts.

2. General structural classification for cuprates

As a whole, the copper–oxygen structural units in copper oxysalt minerals correspond to the classification scheme (Leonyuk *et al.*, 1998) developed for synthetic cuprates grown from melts and fluxes or obtained as a result of solid-state reactions. However, there are some specific features in the structure of minerals, which will be analyzed below.

In the present structural analysis of minerals: (i) the square coordination of Cu^{2+} by O atoms was assumed wherever possible; (ii) the values of the Cu–O distances in the Cu^{2+} polyhedron were taken as the main criterion for a determination of the coordination; (iii) it was assumed that, owing to the stability of the acid complex, isomorphic substitutions are not possible for Cu in the Cu–O complex playing the role of an acid radical; (iv) the salt-forming cation should be present in the complex compound under consideration; (v) in the case of copper–oxygen compounds like CuB_2O_4 , CuGeO_3 , CuSiO_3 , Bi_2CuO_4 , $\text{Cu}(\text{NO}_3)_2$ *etc.*, in which several acid-like Cu–O complexes can be distinguished and there is no additional

atom acting as a salt-forming cation, the atom with a smaller value of electronegativity should play the role of the salt-forming cation. From this point of view, it is possible to define CuB_2O_4 as ‘copper borate’, CuGeO_3 as germanium cuprate *etc.* When the electronegativity values are close, as in Cu and Bi, then the compound can be equally considered in both classes.

Taking into account the latter statement, it is reasonable to analyze the case of malachite, $\text{Cu}_2(\text{OH})_2(\text{CO}_3)$, separately. The structure of malachite (Fig. 1) is composed of CO_3 triangles and chains of dimers, *i.e.* two CuO squares sharing an edge. The carbonate complex obviously possesses an acid character. The chains of dimers are also ascribed to the acid complex, *e.g.* in $\text{Y}_2\text{Cu}_2\text{O}_5$. On the one hand, in malachite, copper should represent the cation owing to its lower value of electronegativity as compared with carbon, leading to weaker Cu–O bonds than C–O. The cation-type role of Cu is confirmed by the possibility of trivalent iron, nickel and aluminium to substitute for Cu in malachite. On the other hand, the Cu–O bonds are strong enough to cause magnetic properties related to the Cu–O complex, as will be shown below. Therefore, it is reasonable to assume that the manifestation of a particular property indicates the presence of a certain Cu–O complex with strong enough inside bonds but does not necessarily define the function of Cu atoms as acid-forming cations.

The structures of a series of copper oxysalt minerals were analyzed making use of the structural data from the ICSD database (*Retrieve*, version 2.01, Gmelin Institute, FIZ, Karlsruhe, Germany). As a result of this analysis, the structural classification scheme for both natural and synthetic cuprates was developed (Table 1).

In most synthetic cuprates, the structural category of isolated (Cu, O) complexes was represented by isolated squares and by the combination of different isolated units (Leonyuk *et al.*, 1998). In copper oxysalt minerals, the isolated

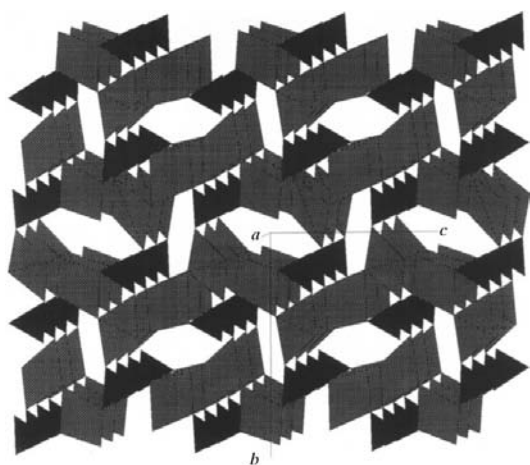


Figure 1
Structural units in malachite, $\text{Cu}_2(\text{OH})_2(\text{CO}_3)$ [space group $P2_1/c$, monoclinic, $a = 3.240$, $b = 11.974$, $c = 9.502$ Å, $\beta = 98.8^\circ$ (Zigan *et al.*, 1977)]. The chains of Cu–O dimers along the c axis are stacked along the a axis forming the ‘wall’. Triangles of CO_3 join the neighbouring chains of Cu–O dimers.

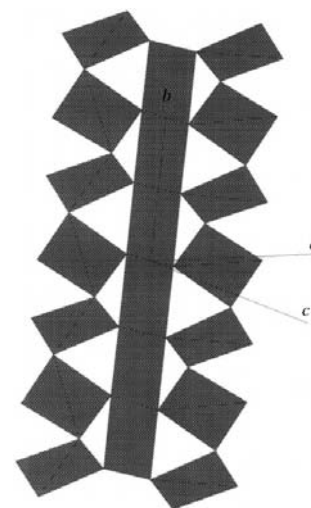


Figure 2
Cu-containing units in the structure of antlerite, $\text{Cu}_3(\text{SO}_4)(\text{OH})_4$ [space group $Pnma$, orthorhombic, $a = 8.244$, $b = 6.043$, $c = 11.987$ Å (Hawthorne *et al.*, 1989)]. The 1D unit is composed of a 1D ribbon and two 1D corrugated chains of CuO squares.

Table 1
Structural systematization of synthetic and natural cuprates.

Structural category of the (Cu ₂ O) complex	Structural unit	Configuration of structural unit	Remarks
Isolated 0D	Isolated square Isolated dimer Cluster	Isolated square or flattened tetrahedron Two CuO squares sharing an edge Spherical cluster of 12 CuO squares sharing vertices	Frequently found (arthurite, turquoise) Callaghanite Tschortnerite
	Combination of several 0D units	Isolated square, ring and cluster of CuO squares	Absent in minerals
1D	Ribbon	CuO squares sharing edges	Frequently found, corrugated
	Chain	Ordinary chain (CuO squares sharing corners) Ribbon-like chain (chain of dimers sharing corners) Double chain Chain of dimers Tube-like chain	Frequently found, corrugated Malachite Absent in minerals
	Combination of 1D units	Combination of ribbon and two corrugated chains	Antlerite
	Combination of 0D and 1D units	Sheet of squares sharing the vertices Sheet of squares sharing edges and corners Sheet of squares sharing edges Chain and ordinary plane Ribbon and ladder-like plane	Absent in minerals
2D	Combination of 1D and 2D units	Sheet of ribbons joined by squares Corrugated ribbons of dimers joined by isolated squares	Cornubite, pseudomalachite Cornetite
	Combination of 0D and 1D units	Perpendicular corrugated ribbons and chains Alternating ribbons and corrugated chains	Likasite Frequently found (botallackite, devilline, ktenasite <i>etc.</i>)
	Combination of two 1D units	Clusters of 12 CuO squares sharing vertices	Absent in minerals
	Combination of 1D and 2D units	Framework of ordinary chain and planes of rings	
3D	Combination of two 1D units oriented in perpendicular directions	Corrugated ribbons and corrugated chains in perpendicular directions	Atacamite

squares, or their distorted versions in the shape of flattened tetrahedra, are frequently found, *e.g.* in arthurite, turquoise, metatorbernite. In addition, two other 0D complexes were found in minerals: (i) an isolated dimer composed of two CuO squares sharing an edge (callaghanite); (ii) a spherical cluster of 12 CuO squares sharing corners (tschortnerite). The latter unit is similar to the clusters forming the framework in Cu₆O₈YCl.

Among 1D structural complexes, two main structural units, the ribbon of CuO squares sharing edges and the chain of CuO squares sharing corners, are frequently found in the structure of oxysalts, *e.g.* ribbons in linarite and chains in fornacite. As a rule, these 1D units are corrugated in minerals.

The other 1D Cu-containing units that have been noticed in synthetic cuprates (Leonyuk *et al.*, 1998) are absent in minerals. However, new complex 1D units were found, such as the combination of 1D ribbons and 1D chains in antlerite (Fig. 2).

The 2D complexes, *i.e.* planes of various types, as well as the combination of 1D and 2D units (Leonyuk *et al.*, 1998), were not found in copper oxysalt minerals. However, a sheet of Cu–O dimers was found in nissonite (Fig. 3). In addition, in minerals, the 2D complexes were formed by the combination of units of various dimensionality. In pseudomalachite and

cornubite (Fig. 4), the 2D sheets are formed by corrugated ribbons, which are combined by the CuO squares. The 2D sheets composed of two 1D units, ribbons and corrugated chains are frequently found in minerals (Fig. 5).

The 3D complexes revealed in synthetic cuprates (Leonyuk *et al.*, 1998) were not found in copper oxysalt minerals. However, the framework of a new type is formed in atacamite. This framework is composed of two 1D units, corrugated ribbons and chains, oriented along perpendicular directions (Fig. 6).

3. Magnetic properties of cuprates

Preliminary studies were carried out (Maltsev *et al.*, 2001) in order to reveal the most general correlation between particular features of magnetic properties and the copper–oxygen motifs in copper oxysalt minerals. The results of magnetic measurements on linarite (Szymczak *et al.*, 2000) and malachite (Janod *et al.*, 2000) were analyzed in more detail together with the specific heat data in order to reveal a possible manifestation of the spin-Peierls effect.

The temperature dependence of magnetic susceptibility $\chi(T)$ was investigated on a series of copper oxysalt minerals with various Cu-containing units. The samples studied were

from the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow.

The temperature dependence of magnetic susceptibility in minerals was analyzed using an $S = 1/2$ isolated anti-ferromagnetic dimer model (Carlin, 1986), which has been used (Baran *et al.*, 1999) for other Cu-containing compounds. In the analysis of the experimental results, the contributions of the free magnetic ions and other possible imperfections were also taken into account as the Curie–Weiss-like term.

With respect to the contribution of dimers, the studied minerals could be divided into two main groups, as described below.

Group A – minerals in which the dimer contribution was clearly indicated. This group of minerals can be subdivided as follows.

(i) The compounds with a relatively strong intradimer interaction. The susceptibility maximum appears at relatively high temperatures (100–150 K). In these minerals, the

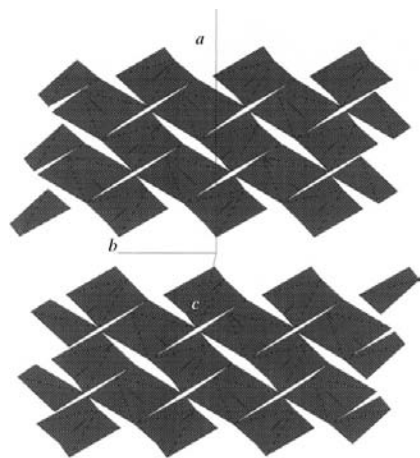


Figure 3
Cu-containing units in the structure of nissonite, $\text{Cu}_2\text{Mg}_2(\text{PO}_4)_2(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ [space group $C12/c1$, monoclinic, $a = 22.523$, $b = 5.015$, $c = 10.506$ Å, $\beta = 99.6^\circ$ (Groat & Hawthorne, 1990)]. 2D units are composed of Cu–O dimers sharing corners.

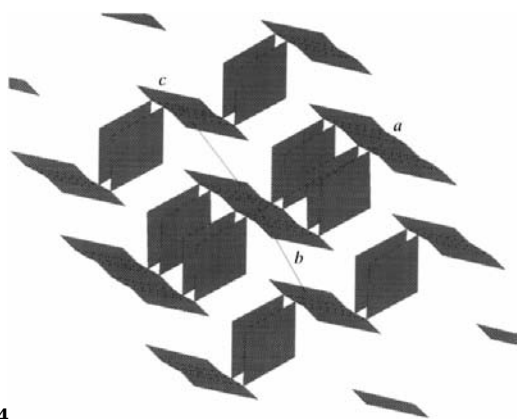


Figure 4
Cu-containing units in the structure of cornubite, $\text{Cu}_5(\text{OH})_4(\text{AsO}_4)_2$ [space group $P1$, triclinic, $a = 6.121$, $b = 6.251$, $c = 6.790$ Å, $\alpha = 92.9$, $\beta = 111.3$, $\gamma = 107.5^\circ$ (Sieber *et al.*, 1984)]. 2D units are composed of corrugated ribbons joined by CuO_4 squares.

presence of natural structural dimers composed of CuO squares sharing edges is to be noted. An example of such compounds is malachite (Fig. 7). At low temperatures, a dominant Curie–Weiss contribution is observed in malachite that can be attributed to a small amount of isolated magnetic ions. A similar dependence of $\chi(T)$ is determined in chalcocite, which, in fact, is not a cuprate and in which only a small part of the Cu atoms is magnetically active.

(ii) The compounds with relatively weak intradimer interactions and a possible contribution from interdimer interactions. In such compounds, the maximum in $\chi(T)$ or a singularity in the shape of a ‘bump’ appear at low temperatures. The maximum in $\chi(T)$ is observed in linarite (Szymczak *et al.*, 2000), caledonite (Fig. 8), botallackite and devilline, whereas the bump is found in serpierite (Fig. 9) and ktenasite. In the two latter minerals, the origin of the Curie–Weiss contribution is not clear because, as follows from the data analysis, the number of ions responsible for this contribution is comparable with those giving a dimer contribution.

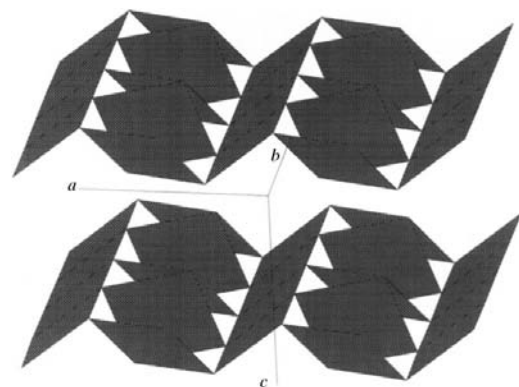


Figure 5
Cu-containing units in the structure of botallackite, $\text{Cu}_2(\text{OH})_3\text{Cl}$ [space group $P2_1/m$, monoclinic, $a = 5.636$, $b = 6.126$, $c = 5.717$ Å, $\beta = 93.1^\circ$ (Hawthorne, 1985)]. 2D sheets are composed of two 1D units, ribbons and corrugated chains.

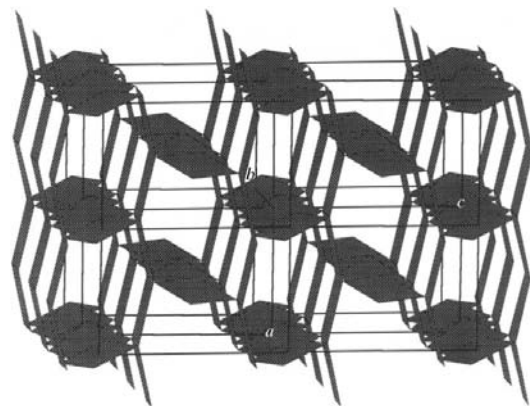


Figure 6
Cu-containing units in the structure of atacamite, $\text{Cu}_2\text{Cl}(\text{OH})_3$ [space group $Pnma$, orthorhombic, $a = 6.030$, $b = 6.865$, $c = 9.120$ Å (Parise & Hyde, 1986)]. The 3D framework is composed of two 1D units, corrugated ribbons and corrugated chains, oriented along perpendicular directions.

Group *B* – minerals in which no clear evidence of dimerization was observed. The examples are posnjakite and eriochalcite. The $\chi(T)$ dependence of eriochalcite (Fig. 10) is well described by the almost pure Curie law. In the case of posnjakite, an abrupt increase of $\chi(T)$ was noticed at $T < 4$ K with a possible maximum at 2.5 K.

The obtained results show that dimer contribution is observed in copper oxysalt minerals containing isolated Cu–O ribbons (linarite), isolated chains (caledonite) and 2D units composed of ribbons and chains (botallackite, devilline, serpierite and ktenasite). No evidence of dimerization was found in eriochalcite $\text{CuCl}_2(\text{H}_2\text{O})_2$, which is not a cuprate as Cu is coordinated by Cl. Strong intradimer interaction was found in malachite and nissanite, which are composed of chains and planes of dimers, respectively. These magnetic data can be compared with those (Kageyama *et al.*, 1999) obtained for isolated dimers in the Sr borate $\text{SrCu}_2(\text{BO}_3)_2$.

Thus, the experimental measurements of temperature dependence of magnetic susceptibility have shown that

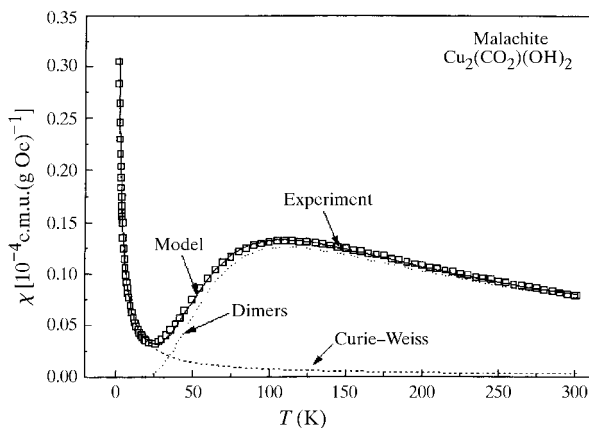


Figure 7 Temperature dependence of the magnetic susceptibility in malachite. Experimental data (points) were described by the model (solid curve), which takes into account the Curie-Weiss (dashed curve) and dimer (dotted curve) contributions.

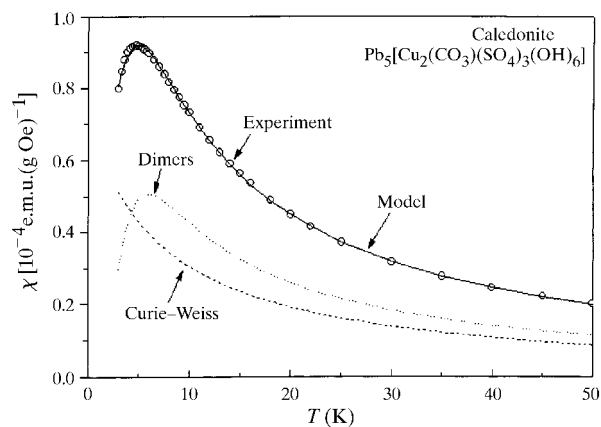


Figure 8 Temperature dependence of the magnetic susceptibility in caledonite. Experimental data (points) were described by the model (solid curve), which takes into account the Curie-Weiss (dashed curve) and dimer (dotted curve) contributions.

magnetic properties are directly related to the particular structure of Cu-containing units. It seems that the dimerization of magnetic moments can be considered as a property of cuprates, which is strongly dependent on the type of the Cu-containing structural unit. An intradimer interaction is strong in minerals with structural dimers whereas it is weak in minerals with homogeneous structural units as 1D ribbons and chains or 2D planes composed of variously polymerized CuO squares.

4. A possible extension of the classification scheme

The structural classification scheme of cuprates presented above, in which copper oxysalt minerals have been included, can be extended by a possible discovery of new structural types. The most important aspect to be noted is that there is no distinct boundary between cuprates, copper oxysalts and Cu-containing complex oxides. In fact, there are three basic types of copper–oxygen compounds: (i) copper oxide (O) in which all O atoms are equally assigned to all cations; (ii) copper salt (S) in which Cu is a salt-forming cation and another atom, X, plays the role of acid-forming cation; (iii) cuprate (C) in which Cu is the acid-forming cation and atom M is the salt-forming cation.

Copper oxysalts (OS) are intermediate between copper oxide and copper salt. Intermediate between copper salts and cuprates are compounds (SC) in which Cu atoms play the roles of salt-forming and acid-forming cations, and ‘double salts’ with two acid-forming cations, X and Cu. Between cuprates and copper oxides there are oxycuprates (OC) or oxysalts of cation M and fragmental structures composed of the blocks characteristic of cuprates and oxides, such as well known $\text{YBa}_2\text{Cu}_3\text{O}_6$ -type compounds. Taking into account the isomorphous substitutions, all Cu-containing high- T_c superconducting should be located on the line cuprate–copper oxide and in the group of cuprates.

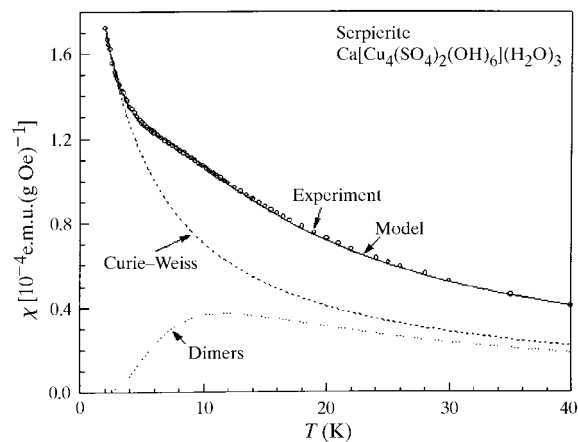


Figure 9 Temperature dependence of the magnetic susceptibility in serpierite. Experimental data (points) were described by the model (solid curve), which takes into account the Curie-Weiss (dashed curve) and dimer (dotted curve) contributions.

It should be noted that the 'triangle' described above is characteristic not only for copper but for many elements as well. However, a realization of the triangle depends on the degree of amphoteric nature for a given element, its charge and size determining the possibility of isomorphism. In this respect, copper is obviously unique.

Two other aspects in a further structural analysis of cuprates should be additionally discussed.

(i) In the structure of complex salts with several acid complexes, so-called 'mixed structural units' should be distinguished.

(ii) The next aspect, the importance of which was emphasized by Belov (1976), is a similarity of geometrical sizes of the acid complexes such as $[\text{NO}_3]^{1-}$, $[\text{BO}_3]^{3-}$, $[\text{BO}_4]^{5-}$, $[\text{CO}_3]^{2-}$, $[\text{SiO}_4]^{4-}$, $[\text{Si}_2\text{O}_7]^{6-}$. This aspect can be used as the basis for the development of a general hierarchy in the analysis of the structure of inorganic salts.

5. Concluding remarks

Taking into account the arguments above, it is reasonable to assume that in copper–oxygen compounds copper can simultaneously play the role of both salt-forming and acid-forming cation owing to its amphoteric character. As proposed by Wells (1986), a large variety of structures are observed. Copper–oxygen compounds are represented by oxides, copper salts and cuprates as the salts of hypothetical copper acids. The great diversity of structures was found in the class of cuprates.

Intermediate-type structures can be formed between these three groups of copper–oxygen compounds. Copper oxysalts

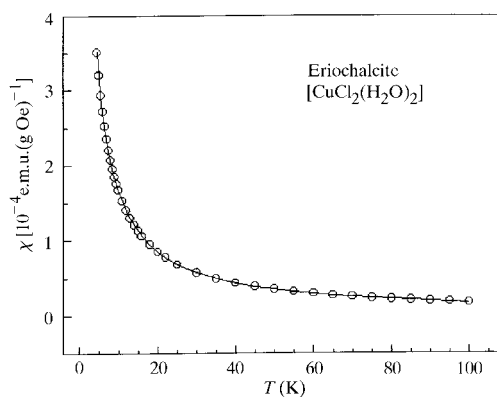


Figure 10
Temperature dependence of the magnetic susceptibility in eriochalcite. Experimental data (points) were described by a pure Curie–Weiss contribution (solid curve).

can be considered as intermediate structures between oxides and salts. The structures with the co-existing units characteristic of oxides and cuprates can also be distinguished, e.g. superconducting cuprates $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$. A particular group between cuprates and copper salts is to be noted. This group consists of Cu–O compounds with Cu playing the role of both salt-forming and acid-forming cation. A common feature between the compounds of this group and intrinsic cuprates is the indication of particular physical properties, e.g. magnetic, related to the structural Cu–O complex.

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