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Polymorphism of Copper(II) Hydroxide

U. W. SCHÖNENBERGER, J. R. GÜNTER, AND H. R. OSWALD

Anorganisch-chemisches Institut der Universität,
Rämistrasse 76, 8001 Zürich, Switzerland

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A small, but sharply defined change in the crystal structure of copper(II) hydroxide has been found at about 60°C. It can be described as an elongation of the *c* axis by 1 % and a shortening of the *b* axis by 0.2 %, the fractional atomic coordinates and the space group remaining unchanged. This phase transition is reversible, showing slight hysteresis, and is connected with an endothermic energy effect of 0.2 kcal/mole. X-ray diffraction and infrared spectroscopy data between room temperature and 100°C are interpreted.

Introduction

The present work was undertaken to reproduce and characterize a change in the crystal structure of copper(II) hydroxide noted in earlier studies on thermal decomposition of this compound (*1*). When copper(II) hydroxide is heated continuously, at about 60°C a sudden and reversible elongation of its *c* axis is found, whereas thermal decomposition to CuO and H_2O occurs only at about 150°C. This effect has now been investigated by means of high-temperature powder X-ray diffraction, infrared spectroscopy at elevated temperatures and differential thermal analysis. The samples used for these experiments were prepared as described by Günter and Oswald (*1*).

High Temperature X-Ray Diffraction

The powder X-ray diffraction diagram of copper(II) hydroxide has been registered continuously from room temperature to 100°C, as well as isothermally at various intermediate temperatures by means of a Guinier–Lenné camera (Nonius, Delft). As an example, Fig. 1 shows such a pattern obtained by heating copper(II) hydroxide to 100°C and cooling to room temperature again.

At about 60°C a sudden shift of all reflections with indices $l \neq 0$ occurs. The reflections of diagrams taken at 25°C and at 100°C respectively show no significant changes in line intensities, so that it may be concluded that the fractional atomic coordinates and the space group, $Cmcm$—D_{2h}^{17}, remain

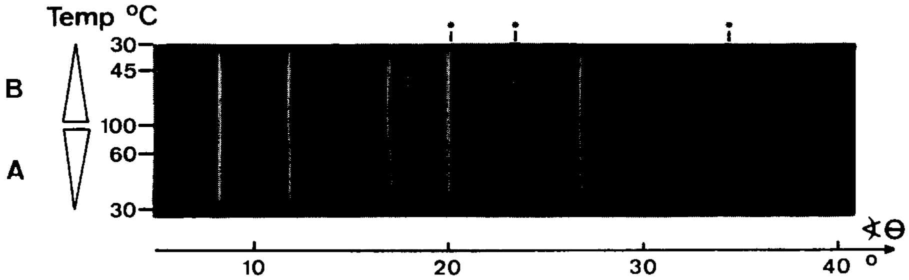

FIG. 1. Powder X-ray diffraction diagram of $Cu(OH)_2$ as a function of temperature.
(A) heating from 30°C to 100°C, line shift at 60°C.
(B) cooling from 100°C to 30°C, line shift at 45°C.
Asterisks indicate platinum reflections from specimen support.

virtually unchanged, while the lattice as a whole is slightly deformed. The amount of this distortion has been determined by refining the complete indexings of powder patterns taken at 25°C and at 100°C by least-squares methods. The following lattice constants have been obtained:

	a	*b*	*c*
25°C:	2.936 ± 0.005 Å	10.54 ± 0.01 Å	5.238 ± 0.008 Å
100°C:	2.936 ± 0.005 Å	10.52 ± 0.02 Å	5.290 ± 0.010 Å

Thus the *c* axis is elongated by 0.05 Å or about 1 %, whereas the *b* axis is very slightly shortened by 0.02 Å or about 0.2 %. The *a* axis remains unaffected within the limit of error.

The crystal structure of copper(II) hydroxide is orthorhombic, containing chains of distorted octahedra along [100], which form layers parallel to (010), corrugated in the direction of the *c* axis (*2*).

From the unchanged intensities it can be concluded that the fractional atomic coordinates remain unaffected by the lattice distortion. Based on this assumption, a polyhedron of oxygen atoms coordinated to one copper atom in the crystal structure of copper(II) hydroxide (*2*) may be drawn for both high and low temperature forms of the hydroxide, and the calculated interatomic distances indicated (Fig. 2).

Main changes occur in the copper–oxygen distances being oriented parallel to the *c* axis, slighter differences in oxygen–oxygen distances forming edges of the coordination polyhedron lying parallel to *b*. As will be shown later, distances from oxygen atoms in an octahedron of one layer to one in the neighbouring layer are also of considerable interest. It can easily be seen that two kinds of such distances, representing possible hydrogen bonds, exist. The first, lying in the (001) plane, remains essentially unaffected, while the other, having a considerable component in the *c* direction, changes from 2.97 Å to 3.00 Å by about 1 %.

Infrared Spectroscopy

Measurements of infrared spectra were made on a Beckman IR 12 spectrometer, using KBr pellets. For use at elevated temperatures, an evacuable "KBr Minidie" from RIIC was slightly modified, so as to be used as an oven for KBr pellets. A thermocouple was pressed directly into the pellet. Spectra were recorded between room temperature and 100°C. Figure 3 gives a schematic representation of such a spectrum taken at 40°C. It gives evidence that the bands between 1300 cm^{-1} and 1500 cm^{-1} found by Cabannes–Ott (*3*) and by Tarte (*4*) must be caused by carbonate impurities in their samples. The bands found in our spectra will subsequently be discussed.

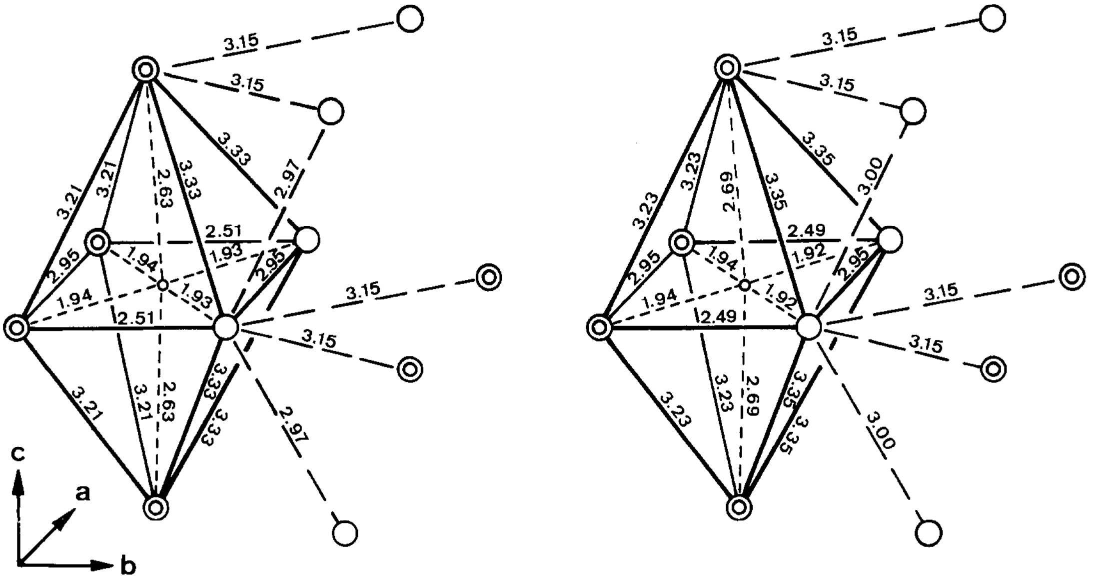

FIG. 2. Coordination polyhedron of a copper atom in the crystal structure of $Cu(OH)_2$.
Left, Interatomic distances at 25°C. Right, Interatomic distances at 100°C.
Small circles: Cu^{2+}, large single circles: OH(I), large double circles: OH(II).

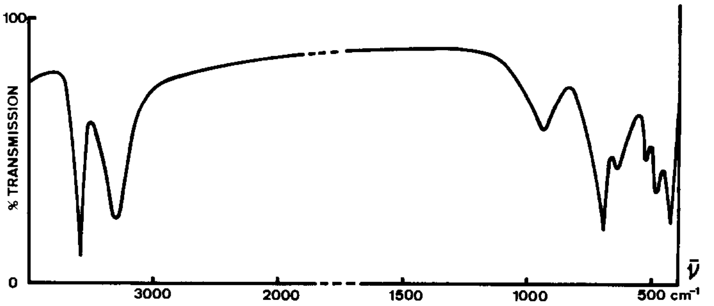

FIG. 3. Infrared spectrum of $Cu(OH)_2$ at 40°C.

Range 2000–4000 cm^{-1}. Only two bands are observed in this region. At 40°C they appear at 3304 cm^{-1} and 3574 cm^{-1} respectively. They can be ascribed to valence vibrations ν_{OH}, caused by OH^- ions hydrogen bonded to different degrees.

When the sample is heated, the band at 3304 cm^{-1} is considerably, but not continuously, shifted as shown in Fig. 4, the largest shift occurring at 53°C.

It corresponds to a decrease in hydrogen bond strength and to an increase in O—H· ·O distance. The lengths of O—H· ·O distances, calculated from Lippincott–Schroeder equations (*5*) change from 2.80 Å to 2.82 Å. The fit of these absolute values with X-ray data is not very close, as this is often the case, but the relative elongations obtained by X-ray and infrared data are of well comparable magnitude.

If the specimen is cooled again, a peculiar hysteresis effect is observed, as the band shift is reversed, but occurs at a temperature of only about 40°C. On reheating, the sudden increase in wavenumber is found at about 44°C.

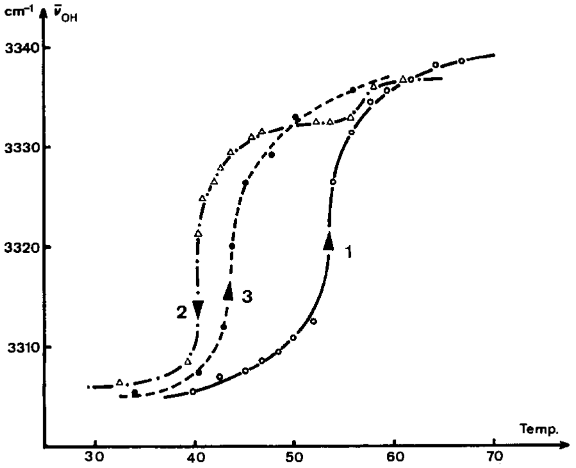

FIG. 4. Temperature dependence of infrared absorption band at 3304 cm^{-1} (room temp.) in consecutive heating (1), cooling (2) and reheating (3) temperature program, showing hysteresis effect.

The shift of the second band is much smaller, from 3574 cm^{-1} to 3581 cm^{-1}, as is expected from X-ray evidence, showing that the second hydrogen bond is only very slightly affected by the phase change.

Range 400–1000 cm^{-1}. At 40°C bands in this range lie at 940, 695, 640, 517, 485 and 420 cm^{-1}. While the first two absorptions are considered to correspond to δ_{OH}, the latter four may be caused by the different Cu-O distances in the structure of copper(II) hydroxide.

Using the empirical equations of Glemser and Hartert (*6*), Cu–O distances may be evaluated from ν_{OH} and δ_{OH} wavenumbers:

ν_{OH}	3304 cm^{-1}	3574 cm^{-1}	3304 cm^{-1}
δ_{OH}	940 cm^{-1}	695 cm^{-1}	232 cm^{-1}
Cu–O$_{Ir}$	2.03 Å	2.07 Å	2.65 Å
Cu–O$_{X\text{-ray}}$	1.93 Å	1.94 Å	2.63 Å

Again the exact values of infrared and X-ray data deviate slightly, but their relative magnitudes agree reasonably well. The deviation may be due to a certain ambiguity of the ionic radius of Cu^{2+}. The value of 0.72 Å used is the one given by Ahrens (*7*).

The only band in this region which is shifted during heating is the one at 640 cm^{-1} (40°C), the wavenumber of which decreases to 608 cm^{-1} (100°C). Therefore it is considered to be connected with the Cu–O distance oriented parallel to *c*, which changes from 2.63 Å to 2.69 Å.

Range 200–400 cm^{-1}. In this region there is one sharp band at 232 cm^{-1} and a broad double band at 332/343 cm^{-1}. The absorption at 232 cm^{-1} can be attributed to a δ_{OH} vibration and has been included in the table given for vibrations in the range 400–1000 cm^{-1}. The bands in this region are

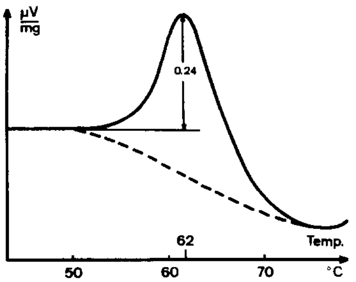

FIG. 5. Differential thermal analysis curve of phase change in $Cu(OH)_2$ at 62°C.

not found to shift considerably, which may be due to the low resolution of the spectrometer in this range.

Differential Thermal Analysis

As X-ray and infrared measurements have indicated, the phase transformation considered is well defined, and therefore it ought to be possible to measure the thermal effect associated. This has successfully been done, using a very sensitive prototype apparatus for differential thermal analysis of Mettler A.G., Greifensee.[1] Figure 5 shows the curve obtained.

The phase change of potassium nitrate at 129°C was used to calibrate the curve, and thus an endothermic effect of $\Delta H = 0.2$ kcal/mole $Cu(OH)_2$ could be calculated. According to Schultze (*8*) the base line shift connected with the transformation can be attributed to a change in c_p of the sample.

The very small amount of the energy change involved in the reaction is consistent with the X-ray data indicating only slight structural alterations.

The peak temperature of the differential thermal analysis plot, 62°C, is considered to be the most exact temperature measurement in our experiments, as temperature measurements in the Guinier–Lenné camera are difficult and inaccurate, while those in the infrared spectrometer may slightly deviate from the real value due to the low concentration of copper(II) hydroxide in the KBr pellets.

Discussion

The results obtained by X-ray diffraction and infrared spectroscopy at elevated temperatures and by differential thermal analysis are consistent with each other, indicating a well defined, sharp though small change in copper(II) hydroxide at about 60°C. The transition is fully reversible, but shows slight hysteresis effects. It has to be considered as a change in the modification of copper(II) hydroxide and can be described as an elongation of the *c* axis by about 1% and a shortening of the *b* axis by about 0.2%, the fractional atomic coordinates and the space group being kept constant. The changes in O—H··O bond lengths originating therefrom are consistent with data obtained from infrared spectra. Differential thermal analysis confirms the nature of the process as a phase transition and shows that it is not a continuous deformation of the unit cell, e.g. by thermal expansion. Moreover, the effect is much too big for such an explanation.

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