

Study of the amorphous product of dehydration of copper(II) sulfate pentahydrate

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Dedicated to Professor S. Škramovský on his 75th birthday

X-ray amorphous $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ which is formed at dehydration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ *in vacuo* was studied. The composition of the dehydration product is not constant, but varies between $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ and CuSO_4 depending on dehydration temperature. All these products have irregular arrangement of ions and water molecules which unlike in crystal $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ are not bonded by bridges with two Cu(II) cations.

В работе изучен рентгеноаморфный $\text{CuSO}_4 \cdot \text{H}_2\text{O}$, образующийся при дегидратации $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ в вакууме. Состав продукта дегидратации не постоянен, а колеблется между $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ и CuSO_4 в зависимости от температуры дегидратации. Все эти продукты имеют неупорядоченное расположение ионов и также молекул воды, которые, в отличие от кристаллического $\text{CuSO}_4 \cdot \text{H}_2\text{O}$, не образуют мостиков между двумя катионами Cu(II).

At dehydration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ the formation of X-ray amorphous [1] monohydrate [2], which differs from crystalline compound by higher enthalpy [3] and larger surface [4], was observed. These properties can be explained either by a small size of the particles which do not yield sharp diffraction lines or by an irregular arrangement of ions and molecules [3]. This paper presents the results of investigation of the amorphous product by spectral methods, which can contribute to clarification of the character of amorphous $\text{CuSO}_4 \cdot \text{H}_2\text{O}$.

Experimental

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{D}_2\text{O}$ were prepared by free recrystallization of the commercial chemicals, or anhydrous sulfate in D_2O . Isothermal dehydration was performed on quartz spiral *in vacuo* 10^{-1} to 10^{-2} Pa. Sample weights were between 200—300 mg and were

rehydration does not exhibit preferential orientation of the particles. Infrared spectra of the final products of dehydration are mutually similar as can be seen from Fig. 2 where for comparison also the spectra of crystalline monohydrate, anhydrous sulfate, and of the product of dehydration of pentahydrate in air with the composition $\text{CuSO}_4 \cdot 0.5\text{H}_2\text{O}$, which is apparently a mixture of CuSO_4 and $\text{CuSO}_4 \cdot \text{H}_2\text{O}$, are presented. Assignment of bands is shown in Table 1 for several typical samples. Extremely large broadening of the bands corresponding to

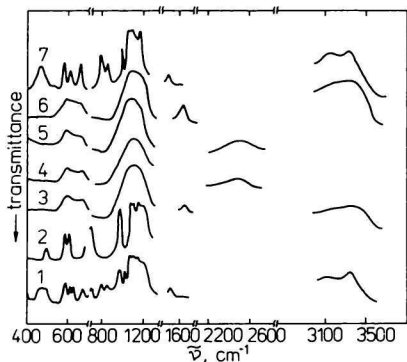


Fig. 2. Infrared spectra of the products of dehydration *in vacuo*.

The spectrum of the product of dehydration in air (bottom curve), crystalline sulfate and monohydrate are also shown for comparison.

1. $\text{CuSO}_4 \cdot 0.5\text{H}_2\text{O}$; 2. CuSO_4 ;
3. $\text{CuSO}_4 \cdot 0.2\text{H}_2\text{O}$; 4. $\text{CuSO}_4 \cdot 0.4\text{D}_2\text{O}$;
5. $\text{CuSO}_4 \cdot 0.7\text{D}_2\text{O}$; 6. $\text{CuSO}_4 \cdot 0.8\text{H}_2\text{O}$;
7. $\text{CuSO}_4 \cdot \text{H}_2\text{O}$.

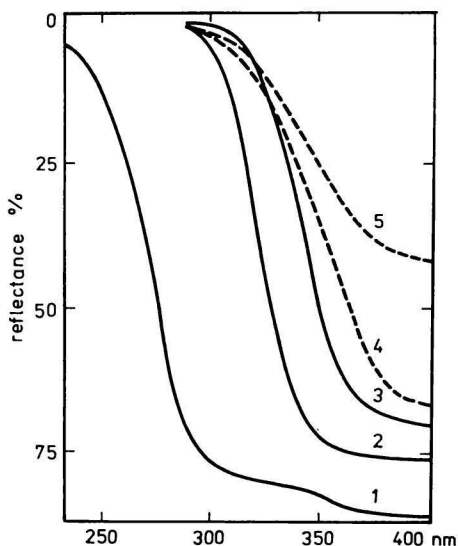


Fig. 3. Diffusion reflection spectra of CuSO_4 , its hydrate and amorphous products in the u.v. region.

1. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; 2. $\text{CuSO}_4 \cdot \text{H}_2\text{O}$;
3. CuSO_4 ; 4. $\text{CuSO}_4 \cdot 0.49\text{H}_2\text{O}$;
5. $\text{CuSO}_4 \cdot 0.26\text{H}_2\text{O}$.

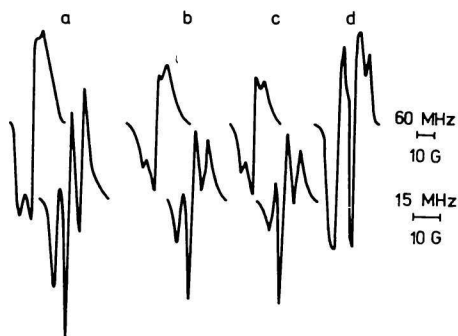


Fig. 4. ^1H -n.m.r. spectra of the amorphous products at 15 MHz (bottom) and 60 MHz; for comparison also spectrum of $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ is shown.

- a) $\text{CuSO}_4 \cdot 0.61\text{H}_2\text{O}$; b) $\text{CuSO}_4 \cdot 0.21\text{H}_2\text{O}$;
- c) $\text{CuSO}_4 \cdot 0.10\text{H}_2\text{O}$; d) $\text{CuSO}_4 \cdot \text{H}_2\text{O}$.

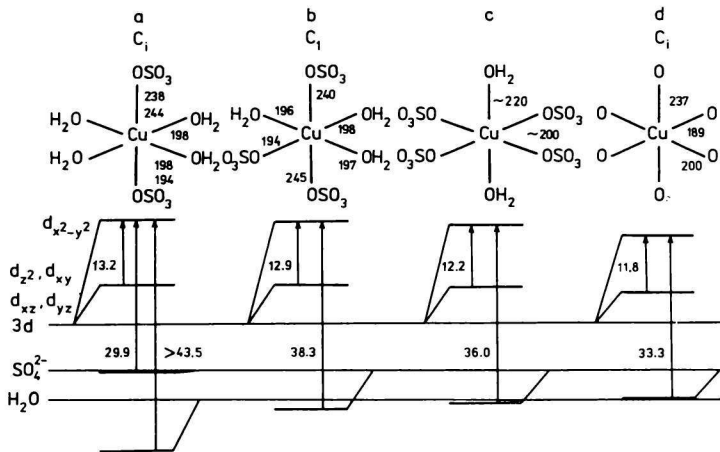


Fig. 5. Environment of Cu(II) and diagram of energy levels in CuSO_4 and its hydrates.

Below the compound formula site symmetry is shown, the distances are in pm, wavenumbers of maxima in 10^3 cm^{-1} ; orbital energies of $3d$ Cu, t_1 (SO_4^{2-}) and b_1 (H_2O) are also presented for comparison.

a) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; b) $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$; c) $\text{CuSO}_4 \cdot \text{H}_2\text{O}$; d) CuSO_4 .

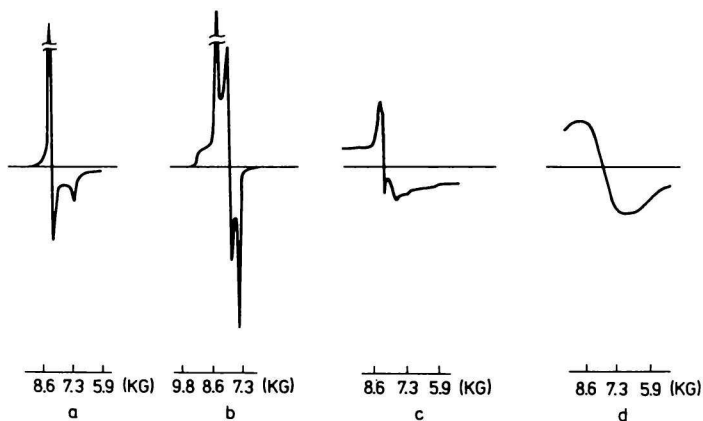


Fig. 6. E.s.r. spectra of cupric sulfate, its lower hydrates and amorphous product dehydrated at 50°C .

a) $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$; b) $\text{CuSO}_4 \cdot \text{H}_2\text{O}$; c) CuSO_4 ; d) amorphous product.

stretching vibrations and partially also to deformation vibration $\nu_3(\text{SO}_4^{2-})$ can be explained by various ways of coordination which cause different shifts and splittings of vibrations of individual anions. Deformation of sulfate groups apparently varies in a broad range, but is practically independent of the water content at least up to the composition $\text{CuSO}_4 \cdot 0.1\text{H}_2\text{O}$. The position of the stretching vibrations $\nu(\text{OH})$ indicates weak hydrogen bridges. Unlike the crystalline monohydrate, in the amorphous products the liberations of water are missing and deformation vibration

Table 1

Infrared spectra of the amorphous products, CuSO_4 , $\text{CuSO}_4 \cdot \text{H}_2\text{O}$,
and assignment of observed bands [5, 8]

Assignment	$\text{CuSO}_4 \cdot \text{H}_2\text{O}$	Amorphous products of dehydration					CuSO_4
		$0.8\text{H}_2\text{O}$	$0.7\text{D}_2\text{O}$	$0.4\text{D}_2\text{O}$	$0.2\text{H}_2\text{O}$	$0.05\text{H}_2\text{O}$	
$\nu_2(\text{SO}_4)$ $\rho(\text{H}_2\text{O})$	478 m					497 w	496 m
$\nu_4(\text{SO}_4)$	593 m 625 m 675 m	601 m 661 sh	600 m 660 sh	600 m 674 sh	600 m 670 sh	591 m 608 m 673 w 705 m	589 m 609 m 710 m
$\rho(\text{H}_2\text{O})$	805 m 870 m						
$\nu_1(\text{SO}_4)$	1020 m					973 m	968 s
$\nu_3(\text{SO}_4)$	1080 s 1120 s 1195 s	1118 s	1110 s	1132 s	1150 s	1095 sh 1165 s	1083 s 1095 s 1155 s 1210 sh
$\delta(\text{H}_2\text{O})$	1510 w	1640 w			1630 w	1625 sh	
$\nu(\text{D}_2\text{O})$			2500 m	2490 m			
$\nu(\text{H}_2\text{O})$	3135 s 3360 s	3390 s			3370 m	3370 w	

s — strong, m — medium, w — weak, sh — shoulder.

$\delta(\text{H}_2\text{O})$ exhibits a distinct shift to higher wavenumbers; it is clear that the bridge bonding of water to two Cu(II) cations, characteristic of monohydrate does not take place in the amorphous products. This may be due also to larger Cu—Cu distance in the products as compared to 0.386 nm in $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ [9].

Diffusion reflection spectra of the amorphous products are similar to those of cupric sulfate and its hydrates. The band corresponding to $d-d$ transitions at 800—1000 nm as well as the band corresponding to CT transitions $p_x \rightarrow 3d_{x^2-y^2}$ in the u.v. region is somewhat broader and with decreasing water content is mildly shifted to longer wavelengths (Fig. 3). It is worth mentioning that the amorphous products with composition $\text{CuSO}_4 \cdot 0.4\text{H}_2\text{O}$ are still distinctly blue while the crystalline monohydrate and anhydrous sulfate are almost white. Wavenumbers of

maxima for crystalline compounds [5] are presented in Fig. 5. Shifts in the spectra agree with the position of H_2O and SO_4^{2-} in spectrochemical sequence and with the optical electronegativity values for H_2O (3.5) and SO_4^{2-} (3.2). Bands of the amorphous products overlap the bands of all crystalline compounds. Shape of the spectra in the u.v. region suggests that a part of sulfate ions in the amorphous products is surrounded by sulfate groups only, while blue colour of the products and slowly decreasing shoulder on the short-wave side of the $d-d$ transitions band suggest on the contrary coordination of larger number of water molecules on another part of cupric cations.

Comparison of the e.s.r. spectra of lower hydrates and of the amorphous product (Fig. 6) confirms that the amorphous product is not a mixture of these compounds and is in agreement with the assumption of different environments of cations. The width of the band at about 2000 G allows only an estimate of g factor in the range 2.1—2.25. The vacuum products are isotropic since the spectra of dehydrated single crystals practically do not depend on orientation.

Results of measurements of surface areas of the amorphous products are summarized in Table 2.

^1H -n.m.r. spectra measured at 15 MHz consist of a narrow central maximum corresponding to more mobile water molecules and broader band which corresponds to more strongly bonded water. It is possible that these maxima correspond to molecules adsorbed on surface and bonded inside the products, since the areas of integrated maxima in Fig. 4 are in approximate agreement with the data in Table 2. The ratio of mobile molecules to rigid ones somewhat increases with increasing dehydration temperature. At 60 MHz frequency both bands strongly overlap. However, the shape of the spectra is quite different from the spectrum of $\text{CuSO}_4 \cdot \text{H}_2\text{O}$, confirming the different ways of water bonding.

Table 2

Surface areas of the amorphous products

In the last column is shown the amount of water in monomolecular layer assuming that one water molecule covers 0.106 nm^2

Dehydration temperature °C	Surface area m^2/g	Total amount of water $\text{mol H}_2\text{O}/\text{mol CuSO}_4$	Water adsorbed on surface $\text{mol H}_2\text{O}/\text{mol CuSO}_4$
40	79.5	0.65	0.22
41	69.5	0.65	0.19
48	81.0	0.58	0.22
60	70.4	0.49	0.18

The existence of amorphous products is probably conditioned by a small mobility of sulfate ions which are coordinated on several different cations and therefore it is difficult for them to regroup in such a way that they fill unoccupied coordination sites formed by removal of water molecules at dehydration. In the amorphous products if compared to $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ at least one apex of coordination polyhedron should be free around each cation due to the different bonding of water. Occupation of these sites by sulfate ions apparently leads to a deformed and metastable arrangement, which at higher temperature or higher water vapour tension which increases mobility of ions [3], regroups to regular crystal lattice. Since the amorphous products are formed also at vacuum dehydration of other hydrates of metal sulfates [4], monohydrates of which have structure similar to that of $\text{CuSO}_4 \cdot \text{H}_2\text{O}$, it is possible to assume in these cases similar mechanism of formation of the amorphous products. However, the difference between crystalline and amorphous compounds is more distinct in cupric compounds, this being probably connected with large variability of internal coordination sphere of cupric cation manifested often by distortion isomerism [10].

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