



Low-temperature heat capacity and thermodynamic functions of natural chalcantite



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ABSTRACT

The heat capacity of natural chalcantite (copper sulfate pentahydrate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) from the deposit Kosmurun has been measured by the method of low-temperature adiabatic calorimetry over the temperature range of (4.3–320) K. The identity of the mineral was proved by methods of XRD, EMPA, IR and Raman spectroscopy. The thermodynamic functions have been calculated based on the experimental data on the heat capacity. The lattice component of heat capacity below 20 K was extracted. The standard values of the heat capacity and entropy for natural chalcantite are as follows: $C_{p,m}^{\circ} = 288.0 \pm 0.4 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$, $S_m^{\circ} = 295.2 \pm 0.8 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$.

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1. Introduction

A natural mineral chalcantite (copper sulfate pentahydrate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) is quite widely spread in the oxidation zones of copper deposits, especially in the arid climate. It is formed as one of the major end products of metamorphism of copper minerals. Due to its high solubility it is a source of copper ions in the geochemical migration of elements. Chalcantite is found in continuous or stalactite forms with a radial fibrous structure. Its color varies from sky-blue to dark blue; crystals are rare and, as a rule, they are small. Iron, sometimes zinc, cobalt and magnesium occur among the main impurities in the mineral.

In Kazakhstan, chalcantite is found in the copper-zinc deposit Kosmurun located in Ayaguz district of Eastern Kazakhstan region, 350 km from the city of Ust'-Kamenogorsk. The oxidation zone in the igneous rocks within the deposit is represented by a small out-lier of the areal crust of weathering (10–30 m thick). On the areas of sulfide mineralization development the thickness of the crust of weathering is 40–50 m. A number of other supergene minerals of copper, zinc, lead and iron is also found there.

Chalcantite is often formed as a secondary mineral in abandoned mines and exhausted pits. Together with ground water this secondary mineral can be carried over for considerable distances

and serve as the basis for formation of copper in other natural compounds. Thus, reliable data on the thermodynamic properties of natural chalcantite are necessary for a number of calculations of geochemical and mineralogical interactions involving this mineral, as well as for various technological processes.

In a well-known reference book of R. Robie and B. Hemingway [1], the thermodynamic properties of chalcantite are given with reference to works [2,3], which, in turn, go back to study [4], based on the measurements performed a few decades ago. In addition, there is a number of known physical and physicochemical studies [5–17] which are mainly related to synthetic samples. The most detailed results of calorimetric and magnetic measurements of a synthetic copper sulfate pentahydrate at the temperature of liquid helium and below are given in [18–22].

Natural chalcantite pentahydrate copper sulfate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ crystallizes in the triclinic system with space group $\bar{P}1$, that is, it has a low degree of symmetry being characterized only by the center of inversion. In [23,24], the parameters of chalcantite unit cell have been determined: the length of the edges $a = 6.141 \text{ \AA}$, $b = 10.736 \text{ \AA}$, $c = 5.986 \text{ \AA}$, degrees of the angles $\alpha = 82.27^\circ$, $\beta = 107.43^\circ$, $\gamma = 102.67^\circ$, and the atomic positions of all the atoms in the structure have also been determined. In an earlier study [25], the unit cell parameters were determined with less accuracy, and the atomic positions of the atoms of hydrogen were not determined. There is also a number of works on synthetic chalcantite dealing with its crystal structure and structural properties

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[26–29]. The results of crystallographic studies show that the presence of the spatial system of copper chains is typical for the crystal structure of chalcantite. The copper chains are available in other minerals of copper, too [30,31], for which the ordering of magnetic moments at low temperatures [32–37] is characteristic.

2. Experimental

2.1. Description of the sample

To carry out the experimental measurements of the heat capacity of a natural sample of pentahydrate copper sulfate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (the Kosmurun deposit, the mountain ridge Genghis of Central Kazakhstan), a monomineral fraction was selected. Sampling of monomineral fraction involved a preliminary dissipation, concentration and selection under a binocular microscope MBS-10 and Carl Zeiss Stemi-2000C with variable magnification (up to $50\times$) of the crystals of the sample containing no visible impurities. The selected crystals of chalcantite have a glassy luster and blue colour. They basically are fragments of irregular shape with an average crystal size less than 1 mm (Fig. 1). In total, about 2.3 g of the test sample was selected for physical and chemical analysis and direct measurements of the heat capacity of the mineral.

The X-ray phase study of chalcantite was carried out on an X-ray diffractometer DRON-2 with Fe-anode. The current parameters: $U_{\text{tub}} = 35 \text{ kV}$; $I_a = 10 \text{ mA}$; the slit parameters: $1.0-1.0-0.25 \text{ mm}$; a rotation speed of a counter $0.25^\circ/\text{min}$. As a reference mark we used reflex (302) of quartz (standard sample of phase composition SOFC 5/84 elaborated by the All-Russia Institute of mineral raw materials VIMS). A weighted portion of a monomineral fraction of the sample for the X-ray measurements was about 0.2 g. Identification of the mineral was carried out according to the position of 54 maxima on the X-ray pattern (Fig. 2) over the range of angles θ from 50° to 3° ($1.3-8 \text{ \AA}$) corresponding to the data on the positions of reflection maxima of chalcantite given in the crystallographic databases of ASTM (card 11–646) and MINCRYST [38]. Most of the experimental peaks have their matching among the lines presented in the database, suggesting that the sample under study is identical to the mineral of chalcantite $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

The spectroscopic studies of monomineral fraction of chalcantite were carried out on an infrared Fourier-spectrometer FSM-1201 (Institute of Organic Synthesis and Coal Chemistry, Karaganda, Kazakhstan) over the range of $450-5000 \text{ cm}^{-1}$ and a Raman spectrometer SPEX TripleMate (Nikolaev Institute of Inorganic Chemistry, SB RAS, Novosibirsk) over the range of $100-1200 \text{ cm}^{-1}$. The resulting spectra are shown in Figs. 3 and 4.

In the experimental IR and Raman spectra of chalcantite we singled out individual absorption bands using the program PeakFit 4.12 [39]. The obtained lines in the IR and Raman spectra of natural chalcantite showed good agreement with the known

experimental data [29,40–49]. In Fig. 3 it is seen that the absorption bands in the IR spectrum of chalcantite in the range of $2000-4500 \text{ cm}^{-1}$ have a complex structure due to a large number of water molecules in the structure of the mineral in symmetrically non-equivalent positions.

To determine the crystal-chemical formula we performed a physicochemical analysis of the main components and trace elements in the monomineral fraction of chalcantite using an electron probe X-ray microanalyser JXA-733 JEOL provided with electron-probe energy-dispersive microanalysis system INCA Energy SEM 300, Oxford Instrument (Satpayev Institute of Geological Sciences, Almaty, Kazakhstan). Resolution 133 eV at 5.9 keV (Mn-cathode), the resolution in the secondary electrons (SEI mode) 7 nm, magnification from 40 to 360,000, the probe current $10^{-12}-10^{-5} \text{ A}$, accelerating voltage 1–50 kV, the elements analyzed: from boron to uranium. A more detailed description of the research of the composition and structure of the samples studied were presented in a previous paper [50].

The content of the main and trace elements in the sample was determined by means of the electron microprobe analysis (Table 1). As it follows from the analysis results, when converting the components to the mole ratios, the major impurities are iron and phosphorus atoms isomorphically entering into the composition of the cationic and anionic groups, respectively.

We think that silicon is contained in the sample mainly as a mechanical impurity in the form of dust and microdisperse particles of sand on the surface of crystals. It is extremely difficult to get rid of these impurities by washing out, because chalcantite itself is soluble in water, but when using other solvents it is possible that water molecules can transit from the crystal structure of the sample into the solution. Isomorphous substitution of sulfates for silicate-ions in minerals is quite uncharacteristic, because, according to the Goldschmidt Rules, ionic radii $\text{S}(+6)$ and $\text{Si}(+4)$ significantly differ, and the difference between electronegativities of these elements is greater than 0.4. Therefore, silicon was not included in the crystal-chemical formula of the compound.

Since the results of thermogravimetric analysis show that the water content in the sample is not fewer than five molecules per molecular unit, we believe that the water content in the sample is equal to the theoretical one. Copper crystal hydrates having a greater water content are not stable in normal atmospheric conditions, and there is no reason to believe that some part of the sample is represented by them. An excess of molar fraction of water in the sample over the theoretical value is 1.009, which can be regarded as being within the measurement uncertainty.

Based on the analysis results of the main and impurity components of the mineral, we found the crystal-chemical formula of the test sample of chalcantite: $\text{Cu}_{0.98}\text{Fe}_{0.02}\{[\text{SO}_4]_{0.99}[\text{PO}_4]_{0.01}\} \cdot 5\text{H}_2\text{O}$. The difference between the relative molecular masses of the mineral calculated by both theoretical and found crystal-chemical formulae is 0.066%.



Fig. 1. Crystals of chalcantite from the Kosmurun deposit: left - magnification $\times 50$, right - magnification $\times 200$.

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