High-Temperature Structural Phase Transition in the LiCu$_2$O$_2$ Multiferroic

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Abstract—The results of thermogravimetric, X-ray diffraction, and electrical studies of LiCu$_2$O$_2$ single crystals in the temperature range 300–1100 K are presented. A reversible first-order phase transition between the orthorhombic and tetragonal phases is found to occur in these single crystals at $T = 993$ K. A pronounced peak on a differential thermal analysis curve and jumps in the unit cell parameters and the electrical resistivity are detected at the phase-transition temperature. The data on the crystal structure of LiCu$_2$O$_2$ and the phase transition-induced change in the entropy determined in this work are used to conclude that the revealed phase transition is caused by the ordering–disordering of Li$^+$ and Cu$^{2+}$ cations in their structural positions.

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1. INTRODUCTION

Crystals LiCu$_2$O$_2 = $ LiCu$^+$Cu$^{2+}$O$_2$ contain the same number of nonmagnetic Cu$^+$ and magnetic Cu$^{2+}$ copper cations with spin $S = 1/2$, which are ordered in lattice positions at room temperature [1, 2]. These crystals are characterized by orthorhombic space group $Pnma$ with lattice parameters $a = 5.730(1)$ Å, $b = 2.8606(4)$ Å, $c = 12.417(2)$ Å, and $z = 4$. The crystal structure of LiCu$_2$O$_2$ consists of Cu–O and Li–O chains along axis $b$, which form LiO$_4$ and CuO$_4$ square networks in the $ab$ planes that are connected by common edges [1]. Along axis $c$, these networks are connected by O$^2$–Cu$^+$–O$^2$– dumbbells (Fig. 1).

The characteristic structural feature of the LiCu$_2$O$_2$ phase, which determines its magnetic properties, is the presence of pairs of exchange-coupled copper–oxygen chains along axis $b$, which form a zigzag ladder structure. Neighboring exchange-coupled chain pairs are far from each other and are separated by chains of Li$^+$ cations and layers of nonmagnetic Cu$^+$ copper (Fig. 1).

LiCu$_2$O$_2$ crystals are used as model objects for studying spin-ladder structures, which exhibit low-dimensional magnetism at low temperatures [3–23]. They undergo a competition of the ferro- and antiferromagnetic exchange interactions of nearest ($J_1$) and next-nearest ($J_2$) spins in CuO$_2$ chains and a strong antiferromagnetic interaction ($J_3$) of spins between neighboring chains ($J_1 = -7.0$ meV, $J_2 = 3.75$ meV, $J_3 = 3.4$ meV [10]). Therefore, LiCu$_2$O$_2$ belongs to the class of frustrated quasi-one-dimensional magnets.

The exchange interactions between Cu$^{2+}$ in the chains cause two sequential magnetic phase transitions at $T_{M1} = 24.6$ K and $T_{M2} = 23.2$ K with the formation of a collinear incommensurate modulated spin structure in the range $T_{M2} - T_{M1}$ and a noncollinear helicoidal incommensurate modulated spin structure below $T_{M2}$ [5, 9, 12, 14–20].

Frustrated magnet LiCu$_2$O$_2$ is a striking representative of improper multiferroics, in which the helicoidal spin structure appearing below $T_{N2}$ initiates macroscopic dielectric polarization $P$ along the $c$ axis of the crystal [11, 14, 15, 19, 20, 22]. These multiferroics exhibit a pronounced magnetoelectric effect and their dielectric polarization can be reversibly reoriented in an applied magnetic field.

Moreover, LiCu$_2$O$_2$ crystals have an electrical instability in the form of electric-field-induced threshold switching from a high- to low-resistance state with specific $S$-like $I$–$V$ characteristics, which contain a segment with a negative differential resistance [24, 25]. Rather low critical switching voltages make these crystals promising for application as active elements in switching devices, controlled inductive element, and relaxation generators.

Additional interest in LiCu$_2$O$_2$ is caused by the fact that the crystal chemistry of this phase resembles that of high-temperature superconducting cuprates [26–28].
Almost all investigations of LiCu$_2$O$_2$ crystals were carried out at low temperatures ($T < 300$ K), and the data on the physical properties of LiCu$_2$O$_2$ at temperatures above room temperature are very scarce. The importance of high-temperature studies is caused by the fact that a crystal structure and its imperfection, which substantially affect the physical properties of crystals, form at high temperatures.

The purpose of this work is to perform high-temperature thermogravimetric and X-ray diffraction powder investigations and to measure the electrical resistivity of LiCu$_2$O$_2$ single crystals. At $T = 993$ K, we detected a reversible first-order phase transition between the orthorhombic and tetragonal phases, which is related to the ordering–disordering of Li$^+$ and Cu$^{2+}$ cations in their structural positions.

2. EXPERIMENTAL

Preparation and Examination of Single Crystals

The LiCu$_2$O$_2$ single crystals to be studied were grown by solution–melt solidification during slow cooling of the $80$CuO $\cdot 20$Li$_2$CO$_3$ melt in alundum crucibles according to the technique described in [24]. The crystals were black and characterized by a lamellar habit with well-developed (001) faces and poorly developed (210) faces. Pronounced cleavage was clearly visible along (001) planes. The crystal sizes reached $4 \times 10 \times 10$ mm$^3$. For thermogravimetric and X-ray diffraction (XRD) studies, some LiCu$_2$O$_2$ single crystals were pounded into powder in an agate mortar.

Phase identification of the single crystals was performed on a Bruker D8 Advance diffractometer using monochromatized $K_{\alpha_1}$ radiation and the Bragg–Brentano focusing scheme. The X-ray diffraction pattern of the powder prepared from the single crystals that was recorded at room temperature (Fig. 2) agrees with the data on LiCu$_2$O$_2$ in [1] and the ICDD database (file PDF 80–2401). All lines in the X-ray diffraction pattern are attributed to the orthorhombic phase (space group $Pnma$, No 62, $a = 5.73$ Å, $b = 2.86$ Å, $c = 12.41$ Å, and $z = 4$ [1]).

Thermogravimetric Studies

These investigations were carried out on a Paulik–Erdei Q-1500D computer-assisted derivatograph. Experimental and standard powder samples were placed in Pt crucibles. As the standard sample, we used an $\alpha$-Al$_2$O$_3$ powder calcined at $T = 1200$°C.

It was found that, when LiCu$_2$O$_2$ was heated in an air atmosphere, the LiCu$_2$O$_2$ phase decomposes into Li$_2$CuO$_2$ and CuO in the range $T = 533–773$ K, which agrees with the data in [24]. The sample mass increment in this case corresponds to the transition of entire Cu$^+$ into the state of Cu$^{2+}$, which supports the stoichiometry of the LiCu$_2^{2+}$Cu$^+$O$_2$ phase in the single crystals under study (Fig. 4a). The sample mass decreases at higher temperatures, in the temperature range of the thermal stability of the LiCu$_2$O$_2$ phase (1163 K $< T < 1323$ K), and this decrease corresponds to the reverse reaction of formation of LiCu$_2$O$_2$ from the products of its decomposition.

When LiCu$_2$O$_2$ is heated in an argon atmosphere, it retains its thermal stability up to the melting temperature (about 1320 K). The DTA (differential thermal analysis) curve has a pronounced endothermic peak at $T_{PT} = 993$ K upon heating, and the sample mass remains unchanged (Fig. 4b). These data demonstrate
that a first-order phase transition takes place at this temperature. Upon cooling, the DTA curve has an exothermic peak at \( T = 983 \text{ K} \), which indicates the reversibility of the phase transition. The recorded DTA peaks are well reproduced during repeated measurements.

Area \( \Delta A \) under a DTA peak during a phase transition can be used to estimate the enthalpy (heat) of the transition,

\[
\Delta H = KM\Delta A,
\]

where \( K \) is the calibration factor and \( M \) is the molar mass. For area calibration, we used the thermogram of a \( \text{BaCO}_3 \) powder recorded under similar conditions and the data on the heat of the phase transition occurring in the \( \text{BaCO}_3 \) phase at \( T = 1079 \text{ K} \) (16.2 kJ/mol) [29]. The specific heat of the phase transition at \( T_{\text{PT}} = 993 \text{ K} \) thus found is 4.05 kJ/mol. Therefore, the change in the entropy during the phase transition detected in \( \text{LiCu}_2\text{O}_2 \) is

\[
\Delta S = \Delta H/T_{\text{PT}} = 4.1 \text{ J/(mol K)} = R\ln(1.7),
\]

where \( R = 8.31 \text{ J/(mol K)} \) is the universal gas constant.

**High-Temperature XRD Studies**

These investigations were carried by powder diffraction analysis in the temperature range 300–1100 K using an Anton Paar XRK900 high-temperature chamber. The experiments were performed in a protective helium gas atmosphere, since the \( \text{LiCu}_2\text{O}_2 \) phase decomposes in air at \( T > 550 \text{ K} \) [24]. To exclude a preferred orientation of crystallites in a powder sample, it was prepared as follows. We formed an \( \text{LiCu}_2\text{O}_2 \) powder suspension in ethanol and applied it onto a Si substrate; after the suspension dried, chaotically oriented crystallites lied on the substrate.

XRD measurements revealed a reversible structural first-order phase transition between the orthorhombic and tetragonal \( \text{LiCu}_2\text{O}_2 \) phases at \( T_{\text{PT}} = 993 \text{ K} \) in heating (983 K in cooling). At \( T_{\text{PT}} \), the temperature dependences of the unit cell parameters exhibit jumplike changes (Fig. 5), and the \((hkl)\) reflections with \( h = 2n + 1 \) that were observed in the X-ray diffraction patterns recorded at \( T < T_{\text{PT}} \) are absent at temperatures above \( T_{\text{PT}} \) (Fig. 2). The detected systematic absences of reflections point to the fact that the primitive space group of symmetry is most probable for the high-temperature tetragonal phase of \( \text{LiCu}_2\text{O}_2 \). The phase-transition temperature determined by XRD agrees with the results of thermal analysis.

An analysis of the high-temperature XRD data shows that the high-temperature phase has tetragonal symmetry with unit cell sizes \( a = 2.8959(4) \text{ Å} \) and \( c = 12.5490(6) \text{ Å} \) at \( T = 1053 \text{ K} \). Thus, during the phase transition into the tetragonal form, unit cell parameter \( a \) approximately halves and becomes equal.
As temperature increases to $T_{PT}$, orthorhombic unit cell parameters $a$, $b$, and $c$ (Fig. 5) increase gradually and almost linearly and the thermal expansion coefficients are $\alpha_a = 11.2 \times 10^{-5}$ 1/K, $\alpha_b = 4.2 \times 10^{-5}$ 1/K, and $\alpha_c = 19.2 \times 10^{-5}$ 1/K. The thermal expansion is rather anisotropic: it is most pronounced along axis $c$ and is less pronounced along axis $b$.

Electrophysical Measurements

We carried out dc and ac (at frequencies of 0.1, 1, 10, 100, 200 kHz) measurements of the electrical resistivity using a computer-assisted LCR/ESR MT4090 (Motech) meter in the temperature range 300–1100 K. For electrophysical investigations, plates with basal planes parallel to (001) and (210) faces were cut from the single crystals. The basal face area and the plate thickness were approximately 10 mm$^2$ and 1–2 mm, respectively. Ag electrodes were applied onto the basal surfaces of the plates by silver paste baking.

Upon heating, electrical resistivity $\rho$ increases gradually until temperature reaches the phase-transition temperature ($T_{PT} = 993$ K), at which the electrical resistivity decreases sharply. Such sharp jumps in the electrical resistivity were observed during measurements in heating and cooling of the crystal both along

![Graph](image_url)

**Fig. 3.** Temperature dependences of the magnetization of LiCu$_2$O$_2$ single crystals measured under FC and ZFC conditions in a magnetic field of 20 Oe.

![Graph](image_url)

**Fig. 4.** Thermograms of a powder made from LiCu$_2$O$_2$ single crystals that were recorded in (a) air and (b) argon atmosphere. DTA is differential thermal analysis, $m$ is the sample mass, $T$ is the temperature, and $t$ is the time. The characteristic temperatures are indicated in the DTA curves.
and across its crystallographic axis \( c \). The electrical resistivity weakly depends on frequency, and the dc and ac electrical resistivities are close to each other. Therefore, assuming that the Ag electrodes block the ionic conductivity component, we conclude that the electron component mainly contributes to the conductivity.

The electrical resistivity exhibits a hysteresis in the temperature range 873–993 K: the values of \( \rho(T) \) upon heating are significantly lower than upon cooling. The temperature dependence of the electrical resistivity in the temperature range \( T = 300–550 \) K has a linear character in the \( \log \rho - (1/T) \) coordinates, and the activation energy calculated in these segments is \( E_a = 0.07 \) and 0.17 eV along and across axis \( c \), respectively.

3. DISCUSSION OF THE EXPERIMENTAL RESULTS

The results of the thermogravimetric, XRD, and electrical resistivity measurements demonstrate that \( \text{LiCu}_2\text{O}_2 \) single crystals undergo a reversible first-order phase transition accompanied by a change in the symmetry from orthorhombic to tetragonal at \( T = 993 \) K. The orthorhombic symmetry of the low-temperature phase is mainly caused by the extension of Cu\(^{2+}\)--O and Li\(^+\)--O chains along axis \( b \). The increase in the symmetry of the initial orthorhombic form to a tetragonal one is possible only due to statistical or ordered redistribution of Cu\(^{2+}\) and Li\(^+\) cations in their structural positions, which results in the averaging of these chains along axes \( a \) and \( b \) so that they become equivalent (see Fig. 1).

![Fig. 5. Temperature dependences of unit cell parameters \( a, b, \) and \( c \) of LiCu\(_2\)O\(_2\).](image)

![Fig. 6. Temperature dependences of electrical resistivity \( \rho \) of LiCu\(_2\)O\(_2\) single crystals measured (a), (c) along and (b), (d) across axis \( c \) in (a), (b) heating and cooling. (1) DC electrical resistivity and (2)–(6) ac electrical resistivity measured at a frequency of 0.1, 1, 10, 100, and 200 kHz, respectively.](image)
therefore, we can conclude that the phase transition under study belongs to order–disorder phase transitions. As follows from the shape of the DTA curve (Fig. 4b), disordering in the Li⁺ and Cu²⁺ sublattices begins with $T = 870$ K as the temperature increases, and the further increase in the temperature is accompanied by a gradual increase in the degree of disorder. This process is sharply completed at the phase-transition temperature ($T_{PT} = 993$ K).

The possibility of mutual replacement of the Li⁺ and Cu²⁺ cations in the crystal structure of LiCu₂O₂ is caused by the closeness of their ionic radii (0.73 Å for Li⁺ and 0.71 Å for Cu²⁺) [31] and the same oxygen surrounding of both cations in the polyhedra of the [MO₅] structure. This disordering of the Li⁺ and Cu²⁺ cations in structural positions was earlier established by XRD analysis at room temperature in single crystals with the chemical formula (Li₀.₂Cu₀.₈)⁺Cu⁺(Li₀.₈Cu₁₂)₂O₃, the composition and structure of which are close to LiCu₃O₃ [32].

As is seen from the results of electrical measurements, the disordering of the cations in the Li⁺ and Cu²⁺ sublattices during the phase transition decreases the electrical resistivity (Fig. 6). The described hysteretic phenomena of the degree of cation disordering upon heating and cooling of the single crystals in the range from $T = 873$ K to $T_{PT}$ cause the hysteresis of the electrical resistivity observed in the same temperature range.

With these results, we can explain the polycrystalline twinning detected in LiCu₂O₂ single crystals [1, 6–11, 13–18]. Obviously, it is related to a decrease in the symmetry from tetragonal to orthorhombic when the crystals are cooled below the phase-transition temperature detected in this work. According to [33], the phase transition accompanied by a change in the crystal symmetry from tetragonal to orthorhombic belongs to ferroelastic phase transitions; therefore, LiCu₂O₂ single crystals can be attributed to ferroelastics. Thus, the multifaceted behavior of LiCu₂O₂ single crystals manifests itself in a combination of magnetic ordering with both ferroelectricity and ferroelastic properties in them.

4. CONCLUSIONS

The high-temperature investigation of LiCu₂O₂ single crystals revealed a reversible first-order phase transition at $T_{PT} = 993$ K. At $T_{PT}$, we detected a clear peak in a DTA curve, a jump of the lattice parameters induced by a change in the symmetry from orthorhombic to tetragonal, and a jumplike change in the electrical resistivity.

The crystal structure of LiCu₂O₂ and the change in the entropy during the phase transition implies that the processes of ordering–disordering of Li⁺ and Cu²⁺ cations in their structural positions are responsible for this phase transition.

The final distribution of these cations in their structural positions depends on the conditions of cooling a crystal from a high temperature to room temperature. The redistribution of Li⁺ and Cu²⁺ cations in their positions breaks the uniformity of a ladder structure but causes exchange coupling between isolated ladder pairs of chains through Cu²⁺ ions having occupied the positions of lithium ions. Therefore, this redistribution should substantially affect the electrical and magnetic properties of the crystals under study. In particular, the authors of [3] reported a substantial change in the magnetic properties and EPR spectra of LiCu₂O₂ crystals after their quenching from high temperatures. Therefore, one should thoroughly control the conditions of preparation of LiCu₂O₂ crystals and, correspondingly, the final distribution of Li⁺ and Cu²⁺ cations in their structural positions in order to obtain reproducible results of studying the physical properties of these crystals.

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