

Structural phase transition in two-dimensional tetramer-cuprate $\text{Na}_5\text{RbCu}_4(\text{AsO}_4)_4\text{Cl}_2$

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Using Raman scattering and optical birefringence we have investigated a low-temperature phase transition in single crystal of the two-dimensional $\text{Na}_5\text{RbCu}_4(\text{AsO}_4)_4\text{Cl}_2$. Phonon anomalies point to a first order nature of the transition. The observed transition is most probably related to a order-disorder transition of the Rb ion positions along the z axis within the ionic framework of mixed alkali metal chloride lattices.

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63.20.-e Phonons in crystal lattices;
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A large part of the motivation to search and study new families of materials with small spin and low dimensionality is based on the discovery of high-temperature superconductivity in the cuprates. Following this line two-dimensional systems with pronounced magnetic fluctuations, competing interactions and structural instabilities have been discovered and investigated [1,2]. Recently a new salt-inclusion copper arsenate $\text{Na}_5\text{RbCu}_4(\text{AsO}_4)_4\text{Cl}_2$ with a remarkable crystal structure was synthesized using a conventional solid-state reaction [3]. This compound exhibits a composite structure of alternating magnetic and insulating layers. The magnetic layer contains $[\text{Cu}_4\text{O}_{12}]^{16-}$ tetrameric units with Cu_4O_4 magnetic cores, which are connected by AsO_4 bridging units. The copper valence state is $2+$, so the Cu ions are magnetic with spin $1/2$. The insulating layer consists of an ionic framework of mixed alkali metal chloride lattices and rarely seen Na_6O_8 clusters. Also the room tempera-

ture crystal structure of $\text{Na}_5\text{RbCu}_4(\text{AsO}_4)_4\text{Cl}_2$ was reported as orthorhombic (space group $Fmmm$, $Z = 2$) [4]. The low-temperature crystal structure, which may have crucial implications for the distinct magnetic order, has not been determined until now. In the Ref. 5 two structural phase transitions around 74 and 110 K seen by ^{87}Rb nuclear magnetic resonance were reported but their nature was not clarified.

To get more insight into the structural phase transitions in $\text{Na}_5\text{RbCu}_4(\text{AsO}_4)_4\text{Cl}_2$ we performed Raman scattering (RS) and birefringence experiments. Experiments on the visual observations of the domain structure formed in the vicinity of the structural phase transition were carried in parallel.

RS measurements were performed in quasi-backscattering geometry with the excitation line $\lambda = 514.5$ nm of an Ar^+ laser. The laser power of 5 mW was focused to a 0.1 mm diameter spot on the sample surface. Raman spec-

tra measured with different laser powers showed that the chosen power is sufficiently small to ensure a negligible heating of the sample. Spectra of the scattered radiation were collected by a DILOR-XY triple spectrometer and recorded by a nitrogen cooled charge-coupled device detector with a spectral resolution of $\sim 1 \text{ cm}^{-1}$. Single crystals are transparent, blue, and plate like with plate surface perpendicular to b axis. Typical crystal dimensions are $3 \text{ mm} \times 1 \text{ mm} \times 200 \text{ }\mu\text{m}$.

The linear optical birefringence

$$\Delta n = \delta\lambda/2\pi t, \quad (1)$$

where δ is the phase shift between the linearly polarized optical eigenmodes of the crystal, and t is the thickness of the crystal, was measured in an optical helium cryostat. In the experiments a quarterwave plate was used as the compensator to measure the birefringence. In this case, δ was defined accurate to $2\pi k$ where $k = 0, 1, 2, \dots$. A filament lamp and an interference filter with a pass band of 11 nm width were used as a light source. Measurements were carried out with the wavelength of $\lambda = 515 \text{ nm}$.

For the visual observations of the domain structure formed in the vicinity of the structural phase transition a polarizing optical microscope was used.

The group-theoretical analysis of the Γ -point Raman-active phonon modes for the orthorhombic $\text{Na}_5\text{RbCu}_4(\text{AsO}_4)_4\text{Cl}_2$ is presented in Table 1. Of the total 186 Γ -point phonon modes, 99 modes ($29A_g + 25B_{1g} + 21B_{2g} + 24B_{3g}$) are Raman-active. In Fig. 1, we show the polarized Raman spectra of $\text{Na}_5\text{RbCu}_4(\text{AsO}_4)_4\text{Cl}_2$ at room temperature. The sharpness of observed lines is evidence for the high quality of the studied samples. Experimental values of the Raman frequencies are summarized in Table 2. The number of Raman-allowed modes (99) is

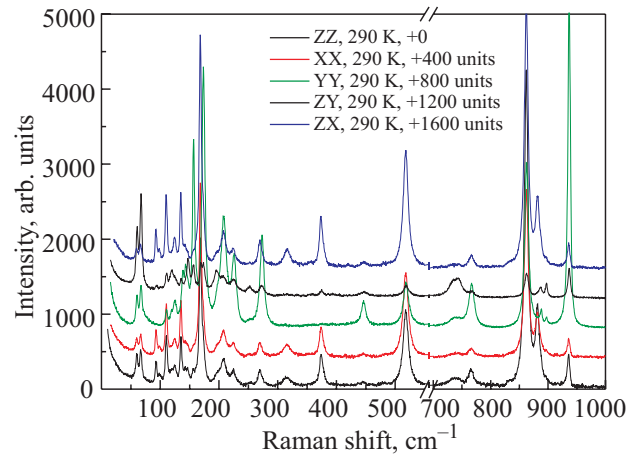


Fig. 1. Polarized room temperature Raman spectra of a $\text{Na}_5\text{RbCu}_4(\text{AsO}_4)_4\text{Cl}_2$ single crystal.

three times larger than the number of experimentally observed lines (33) in the frequency region of $0\text{--}1000 \text{ cm}^{-1}$. It is practically impossible to further analyze the vibrations in such a low-symmetry structure with a large number of partially overlapping Raman-active modes at room temperature.

The most characteristic Raman features related to the structural phase transition with decreasing temperature are the sudden splitting of some phonon modes and the appearance of new modes. In Fig. 2 an examples of observed changes in the Raman spectra with temperature are shown. Intuitively the character of changes allows us to suggest a first order nature of the phase transition. Earlier the structural phase transition at $T = 74 \text{ K}$ in $\text{Na}_5\text{RbCu}_4(\text{AsO}_4)_4\text{Cl}_2$ was related to a change of the local symmetry at the Rb sites [5].

Table 1. Wyckoff notations and Raman irreducible representations for the atoms in orthorhombic $\text{Na}_5\text{RbCu}_4(\text{AsO}_4)_4\text{Cl}_2$ (space group at room temperature is $Fmmm$ N69 [3])

Atom	Wyckoff notation	Γ_{Raman}
Rb(1)*	8 g	$1A_g(xx, yy, zz) + 1B_{1g}(xy) + 1B_{2g}(xz) + 0B_{3g}(yz)$
Rb(2)*	16 n	$2A_g(xx, yy, zz) + 1B_{1g}(xy) + 2B_{2g}(xz) + 1B_{3g}(yz)$
As(1), O(3), O(4)	16 o	$2A_g(xx, yy, zz) + 2B_{1g}(xy) + 1B_{2g}(xz) + 1B_{3g}(yz)$
As(2), O(1), O(2)	16 m	$2A_g(xx, yy, zz) + 1B_{1g}(xy) + 1B_{2g}(xz) + 2B_{3g}(yz)$
Cu, O(5), O(6)	32 p	$3A_g(xx, yy, zz) + 3B_{1g}(xy) + 3B_{2g}(xz) + 3B_{3g}(yz)$
Na(1), Cl(1)	8 h	$1A_g(xx, yy, zz) + 1B_{1g}(xy) + 0B_{2g}(xz) + 1B_{3g}(yz)$
Na(2)	16 n	$2A_g(xx, yy, zz) + 1B_{1g}(xy) + 2B_{2g}(xz) + 1B_{3g}(yz)$
Na(3)	16 k	$1A_g(xx, yy, zz) + 2B_{1g}(xy) + 1B_{2g}(xz) + 2B_{3g}(yz)$
Cl(2)	8 d	$0A_g(xx, yy, zz) + 0B_{1g}(xy) + 0B_{2g}(xz) + 0B_{3g}(yz)$

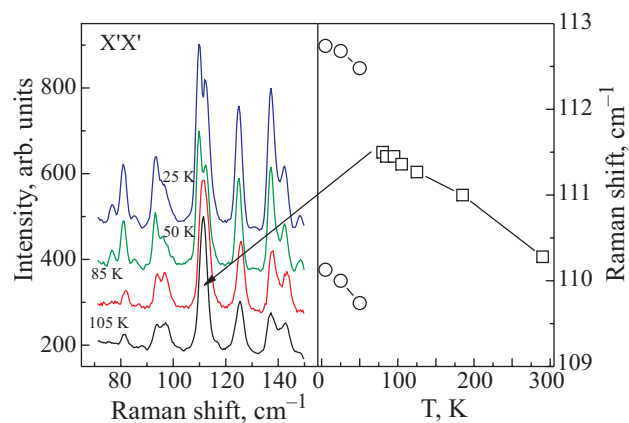
* According to the data [1] the refined occupancies for Rb(1) and Rb(2) are 45 and 27.5%, respectively, to have a total of 100% occupancy with two Rb ions per primitive cell. Total: $\Gamma_{\text{Raman}} = 29A_g(xx, yy, zz) + 25B_{1g}(xy) + 21B_{2g}(xz) + 24B_{3g}(yz)$.

Table 2. Energy of the measured Raman modes in $\text{Na}_5\text{RbCu}_4(\text{AsO}_4)_4\text{Cl}_2$ at room temperature in wave numbers (cm^{-1})

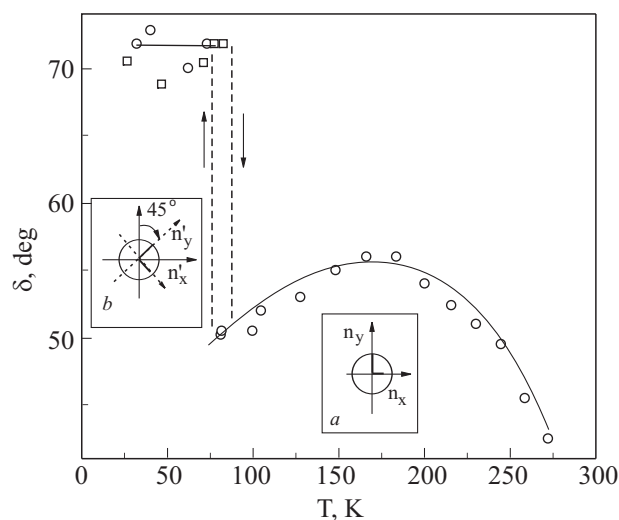
<i>aa</i>	<i>cc</i>	<i>ca</i>	<i>bb</i>	<i>cb</i>
60.1	60.1	60.1	60.1	60.1*
67.0	67.0	67.0	67.0	67.0
92.9	92.9	92.9		92.9
98.6	98.6	98.6*		98.6
110.1	110.1	110.1	110.1	110.1
			119.2	119.2*
124.5	124.5	124.5*	124.5	124.5
135.4	135.4	135.4		135.4
			138.3	
142.9	142.9	142.9	142.9*	142.9
147.3	147.3	147.3	147.3	147.3*
156.8	156.8	156.8	156.8*	156.8
168.5	168.5	168.5*	168.9	168.5
173.5	173.5	173.5	173.5*	173.5
196.8	196.8	196.8	196.8	196.8
207.7	207.7	207.7	207.7*	207.7
224.7	224.7	224.7	224.7*	224.7
252.3	252.3	252.3	252.3	252.3
269.9	269.9	269.9		
			273.3*	273.3
315.9	315.9	315.9		
374.3	374.3	374.3		
			445.7*	
518.2	518.2	518.2	518.2	518.2*
734.5	734.5	734.5	734.5	734.5*
744.8	744.8	744.8	744.8	744.8*
766.6	766.6	766.6	766.6*	766.6
832.6	832.6	832.6		
862.3	862.3	862.3	862.3	862.3
881.9	881.9	881.9		
			887.1	887.1
			897.3	897.3
935.5	935.5	935.5		
			936.6	936.6

* most intensive lines

Visual studies and investigation of temperature dependence of birefringence allows us to define more precisely the order of the structural phase transition in $\text{Na}_5\text{RbCu}_4(\text{AsO}_4)_4\text{Cl}_2$. In Fig. 3 the temperature de-


 Fig. 2. Temperature dependence of Raman spectra of $\text{Na}_5\text{RbCu}_4(\text{AsO}_4)_4\text{Cl}_2$ and temperature dependence of phonon energies.

pendence of birefringence is presented. Our experiments point to a small increase of δ with decreasing temperature up to 174 K. A further decreasing of temperature lead to δ decreasing and at $T = 73$ K there is a sharp increase of δ which corresponds to a first order structural phase transition. In the low-temperature phase the axes of optical indicatrix of the crystal (inset *b* in Fig. 3) are turned by an angle of 45° relative to axes of optical indicatrix before the phase transition (inset *a* in Fig. 3). At temperatures below the phase transition the value of δ changes weakly. By substituting $t = 200 \mu\text{m}$, $\delta = 70.4^\circ$, $\lambda = 515 \text{ nm}$ into Eq. (1), we obtain $\Delta n \approx 10^{-3}$ at $T = 32 \text{ K}$. On heating the phase transition occurs at $T = 83 \text{ K}$. Thus, the temperature hysteresis of birefringence by value of about 10 K is observed at the first order phase transition in the crystal of $\text{Na}_5\text{RbCu}_4(\text{AsO}_4)_4\text{Cl}_2$.


 Fig. 3. Temperature dependence of δ in the $\text{Na}_5\text{RbCu}_4(\text{AsO}_4)_4\text{Cl}_2$ single crystal. Insets show sections of the optical indicatrix of the crystal before (*a*) and after (*b*) structural phase transition.

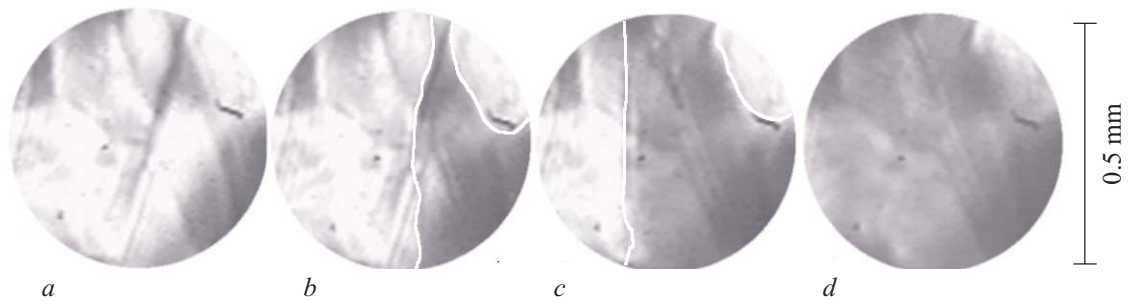


Fig. 4. The two-phase domain structure formed at structural phase transition in the crystal of $\text{Na}_5\text{RbCu}_4(\text{AsO}_4)_4\text{Cl}_2$. The temperature varies from 82.5 K (a) up to $T = 72.5$ K (d). Light line shows the border between crystal phases (b,c).

As it is mentioned above the first order phase transition in $\text{Na}_5\text{RbCu}_4(\text{AsO}_4)_4\text{Cl}_2$ is related to a sharp increase of birefringence and to a rotation of the optical indicatrix axes by 45° . Due to this it is possible to investigate the two-phase crystal domain structure formed at the phase transition visually in polarized light. In Fig. 4,a the image of the investigated sample before phase transition ($T = 82.5$ K) is presented. In this photo dark areas are due to defects of the sample. With decreasing temperatures the new crystal phase forms in the crystal (Fig. 4,b). In this photo the boundary between crystal phases is shown by a light line. With further decreasing of temperature the area of a new phase increases (Fig. 4,c). And at last, at $T = 72.5$ K, the phase transition is completed (Fig. 4,d).

In order to discuss the possible symmetry of the new phase one should mention that due to the large size of the primitive cell with a large number of ions we can not expect a drastic change in the primitive cell volume under structural phase transition. The minor change of Raman spectra evidences also that not so much lattice degrees of freedom are affected by structural phase transition. Moreover, due to this reason the space group of low-temperature phase should demonstrate a subgroup connection with $Fm\bar{3}m$ space group of the high-temperature phase. The 45° rotation of the optic indicatrix and the absence of optical activity in low-temperature phase give some hints about this connection.

Some candidate for the driving force of the structural phase transition can be an uncertainty in the Rb ions positions which is defined at room temperature [3]. Interestingly, that high symmetry $8g$ Rb(1) position with occupancy 45% and main representative coordinates (0.1521(5),0,0) is refined isotropically, while the low symmetry $16n$ Rb(2) position with occupancy 27.5% and main representative coordinates (0.1492(3), 0, 0.0443(4)) is refined anisotropically [3]. The last one demonstrates the tendency for Rb ions to be shifted along z axis. However, the complete occupancy of the $16n$ position is impossible because it violates the allowed number of Rb ions per primitive cell. While the shift of Rb ions in the

fully occupied $8g$ position along z or y directions leads to the lowering of symmetry from orthorhombic to monoclinic. Supposing a first order structural phase transition from low-temperature to high-temperatures as a transition from order to disorder at the Rb sites one can choose the highest subgroup of the space group $Fm\bar{3}m$ that conserves inversion center, number of structural units per cell, and includes the shift of Rb ions along z axis. This subgroup is $C2/m$ space group with unique axis along b direction of the high-temperature phase space group $Fm\bar{3}m$ [6]. One of the in-plane $C2/m$ axes coincides with x axis of the $Fm\bar{3}m$ group, while another one should be directed along $(-1,0,1)$. In the absence of monoclinic distortions, due to small rhombicity, it rotates on 45.36° from z axis of the high-temperature phase. This angle slightly deviates from 45.36° in the presence of monoclinic distortions.

Raman data also support the proposed model. The apparent changes of spectra occur in the low-frequency region, to which the heaviest ions (Rb and As) mainly contribute. Whereas, the high-frequency region which is formed by the vibrations of light complexes like Na_6O_8 and others does not demonstrate anomalies.

In conclusion, using Raman scattering and optical birefringence we have shown that first-order phase transition in $\text{Na}_5\text{RbCu}_4(\text{AsO}_4)_4\text{Cl}_2$ can be related to an order-disorder transition of the Rb ion positions along the z axis.

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