

ISOABSORPTION AND ELECTRICAL STUDIES OF $\text{Cu}_6\text{PS}_5\text{X}$ ($\text{X}=\text{Br}, \text{I}$)
CRYSTALS AT THE FERROELASTIC PHASE TRANSITION

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Temperature dependence of positions of the absorption edge E_g^α ($\alpha = 550 \text{ cm}^{-1}$) of $\text{Cu}_6\text{PS}_5\text{X}$ ($\text{X}=\text{Br}, \text{I}$) crystals in the temperature range 77 to 323 K are studied by isoabsorption measurements. Temperature variation of the total electric conductivity in the range of the second-order ferroelastic phase transition are analyzed.

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1. Introduction

$\text{Cu}_6\text{PS}_5\text{X}$ ($\text{X}=\text{Br}, \text{I}$) crystals are the most extensively investigated among the argyrodite family compounds, known as fast-ion conductors and ferroelastics, having a variety of important physical characteristics [1,2]. They undergo two phase transitions (PT) below the room temperature, one of which being superionic (at temperature T_s), the other - ferroelastic (at temperature T_c) [2]. At room temperature, they are crystallized in cubic syngony ($F\bar{4}3m$ space group) [3]. Below the temperature of the ferroelastic PT $\text{Cu}_6\text{PS}_5\text{Br}$ crystals belong to the monoclinic syngony (Cc space group) and the superionic PT seems to be an isostructural transformation [3]. In the vicinity of the PT, anomalous behaviour of specific heat, dielectric constants, elastic and optical (Raman scattering, birefringence, optical absorption) properties is observed in $\text{Cu}_6\text{PS}_5\text{X}$ ($\text{X}=\text{Br}, \text{I}$) crystals [2,4-7].

Studies of absorption edge in $\text{Cu}_6\text{PS}_5\text{X}$ ($\text{X}=\text{Br}, \text{I}$) crystals have shown exciton absorption bands to be observed at $T < T_s$ [2]. In the vicinity of the superionic PT, the bands undergo considerable changes which are caused by dynamic structural disordering of the copper cation sublattice. At $T > T_s$, at the absorption edge, the exponential parts appear, as described by the Urbach rule [2].

The analysis of the temperature behaviour of the Urbach absorption edge has shown a change of the character of the temperature dependence of optical pseudo-gap and absorption edge energy width to be observed at the ferroelastic PT. Besides, in the range of the ferroelastic PT, the parameters of the exciton(electron)-phonon interaction (EPI), namely the EPI constant and the energy of the effective phonon participating in the absorption edge formation, are changed. The coordinates of the Urbach absorption edge convergency point in the crystals under investigation remain unchanged at the transition from the paraelastic to the ferroelastic phase.

The present research is aimed at studying the temperature variation of optical absorption edge energy position and total electric conductivity of $\text{Cu}_6\text{PS}_5\text{X}$ ($\text{X}=\text{Br}, \text{I}$) crystals in the vicinity of the second-order ferroelastic phase transition.

2. Experimental

$\text{Cu}_6\text{PS}_5\text{X}$ ($\text{X}=\text{Br}, \text{I}$) crystals were obtained by the chemical transport reactions method. The isoabsorption studies of the optical absorption edge were carried out in the temperature range from 77 to 323 K. The studies consisted in investigation of the temperature behaviour of the absorption edge energy position E_g^α at fixed absorption levels $\alpha = \text{const}$. The measurements were carried out for the samples oriented at room temperature in cubic phase, with the light beam propagating along the [100] crystallographic direction. The experimental setup and technique are described in Ref. [2].

3. Results and discussion

3.1. Isoabsorption studies of $\text{Cu}_6\text{PS}_5\text{X}$ ($\text{X}=\text{Br}, \text{I}$) crystals

The isoabsorption measurements have shown that in the range of the superionic PT, being of the first order, a step in $E_g^\alpha(T)$ behaviour is observed, while in the range of the ferroelastic PT, being of the second order, a typical change of the slope in the $E_g^\alpha(T)$ plot is revealed in $\text{Cu}_6\text{PS}_5\text{I}$ crystals (Fig.1). The values of $E_g^\alpha(T)$ in paraelastic phase ($T > T_c$) can often be well described in a framework of the Einstein model by the relation [8]

$$E_g^\alpha(T) = E_g^\alpha(0) - S_g k \theta_E \left[\frac{1}{\exp(\theta_E/T) - 1} \right], \quad (1)$$

$E_g^\alpha(0)$ being the absorption edge energy position at $T = 0$ K, S_g a dimensionless constant, θ_E the Einstein temperature corresponding to the average frequency of phonon excitations of a system of non-coupled oscillators. It should be noted that a sharp anomaly, observed in the superionic PT range in $\text{Cu}_6\text{PS}_5\text{I}$ crystal, is smeared with the I → Br substitution (Fig. 1), what is explained by the increase of the effect of structural disordering [2].

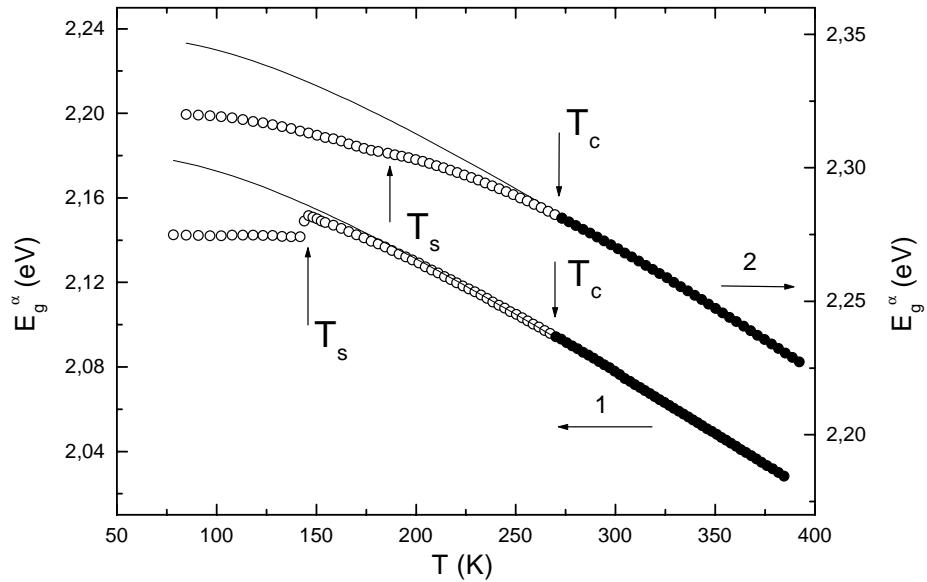


Fig. 1. Temperature dependence of the absorption edge energy position E_g^α ($\alpha = 550 \text{ cm}^{-1}$) for (1) $\text{Cu}_6\text{PS}_5\text{I}$ and (2) $\text{Cu}_6\text{PS}_5\text{Br}$ crystals.

According to Ref. [9], the energy gap variation can be expanded into a series of even degrees of the PT order parameter η . Being restricted by the first term of the expansion, it is given by

$$\Delta E_g^\alpha = a\eta^2, \quad (2)$$

where a is the expansion coefficient. In the crystals under investigation, the nature of the PT order parameter, its dimensionality and number of components, unfortunately, have not been unambiguously determined yet. However, this PT is known to be an improper ferroelastic transition [4], the spontaneous deformation is not the order parameter, but arises due to the nonlinear relationship with the order parameter, the role of the latter being played by some other physical quantity.

In order to calculate the increment $E_g^\alpha(T)$, arising in the ferroelastic phase ($T < T_c$), the experimental dependence of $E_g^\alpha(T)$, in the paraelectric phase ($T > T_c$) was approximated by Eq. (1). Thus obtained curves are shown in Fig. 1 by solid lines. Then the experimental values $E_g^\alpha(T)$ were subtracted from the calculated curve. The $\Delta E_g^\alpha(T)$ dependence for $\text{Cu}_6\text{PS}_5\text{X}$ ($\text{X}=\text{Br}, \text{I}$) crystals is shown in Fig. 2. Since [10]

$$\eta \sim \tau^\beta, \quad (3)$$

then

$$\Delta E_g^\alpha \sim \tau^{2\beta}, \quad (4)$$

where $\tau = (T_c - T)/T_c$ and β is a critical index. In accordance with the Landau theory $\beta = 0.5$. The tangent of the $\log(\Delta E_g^\alpha) = f(\log \tau)$ plot permitted the determination of the power index, and, accordingly, of the β value. The corresponding dependence is shown in the insert of Fig. 2 and the calculated values of β_{opt} are listed in Table 1.

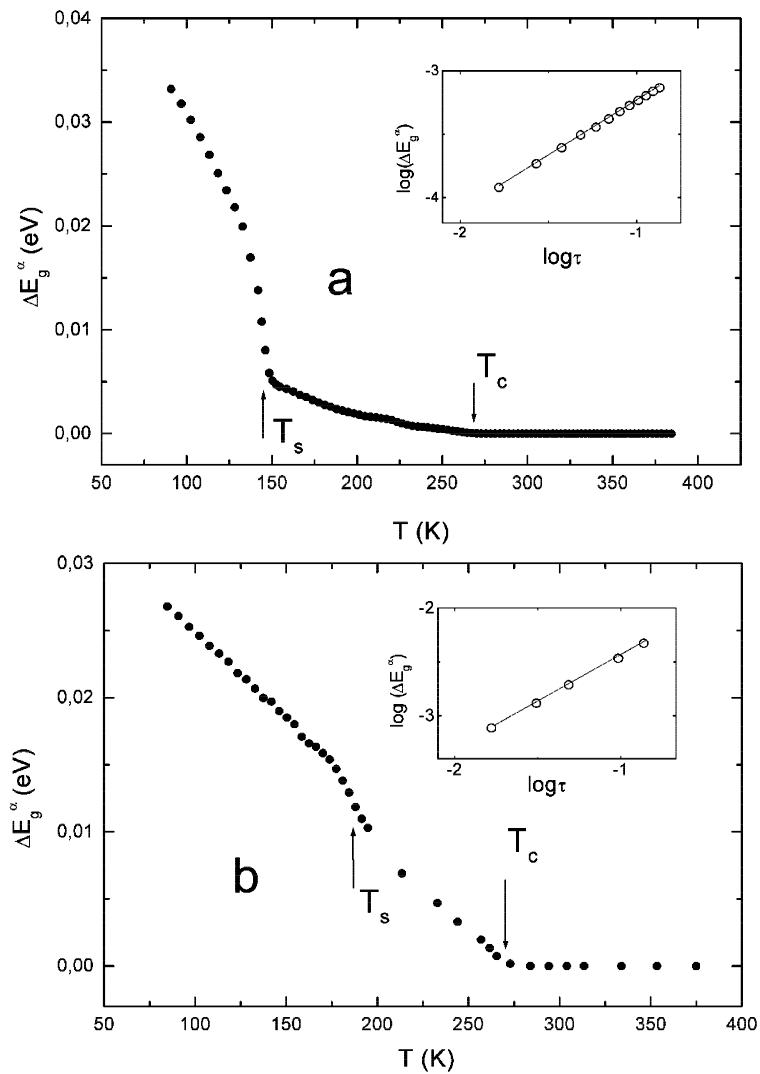


Fig. 2. Temperature dependence of variation of the absorption edge energy position ΔE_g^α for (a) $\text{Cu}_6\text{PS}_5\text{I}$ and (b) $\text{Cu}_6\text{PS}_5\text{Br}$ crystals. The inserts show the dependence of $\log(\Delta E_g^\alpha) = f(\log \tau)$.

TABLE 1. The values of the pre-exponential factor A and conduction activation enthalpy H_a for paraelastic and ferroelastic phases, and critical indices β_{el} and β_{opt} of the order parameter in $\text{Cu}_6\text{PS}_5\text{X}$ ($\text{X}=\text{Br}, \text{I}$) crystals.

Crystal	Temperature range	H_a (eV)	A ($(\Omega\text{cm})^{-1}$)	β_{el}	β_{opt}
$\text{Cu}_6\text{PS}_5\text{Br}$	$T < T_c$	0.5069	1.38×10^6	0.423 ± 0.003	0.428 ± 0.003
	$T > T_c$	0.4465	1.09×10^5	—	—
$\text{Cu}_6\text{PS}_5\text{I}$	$T < T_c$	0.3001	5.33×10^4	0.437 ± 0.005	0.431 ± 0.003
	$T > T_c$	0.2352	3.45×10^3	—	—

3.2. Analysis of temperature dependence of conductivity of $\text{Cu}_6\text{PS}_5\text{X}$ ($\text{X}=\text{Br}, \text{I}$) crystals

The $\ln(\sigma T) = f(10^3/T)$ plots, based on the experimental values of total electric conductivity, obtained in Ref. [11] at the frequency of 100 Hz, are shown in Fig. 3. In the ferroelastic PT range, knees are observed at the plots, what is typical for the second-order PT. The linear character of the temperature dependence of conductivity indicates the thermoactivation character of the latter. To analyze the temperature variation of the electric conductivity, a phenomenological approach is used, which had been earlier successfully applied for protonic and silver-containing superionic conductors [12].

In the case of ionic conductivity, its temperature dependence is known [12] to be described by the relations:

$$\sigma = \sigma_0 \exp\left(-\frac{\Phi_a}{kT}\right) = \frac{A}{T} \exp\left(-\frac{H_a}{kT}\right), \quad (5)$$

$$\Phi_a = H_a - TS_a, \quad A = T\sigma_0 \exp\left(\frac{S_a}{k}\right), \quad \sigma_0 = \frac{e^2 l^2 w n_i \nu_0}{kT}, \quad (6)$$

Φ_a being the thermodynamical activation potential, H_a the activation enthalpy, S_a the activation entropy, A a pre-exponential factor, e the elementary charge; l the ion displacement due to an elementary hop, n_i the number of mobile ions per unit volume, ν_0 the frequency of the ion vibrations in the equilibrium position and w the probability of the ion to be located at a given site provided the adjacent site is free.

By fitting the measured temperature dependence by Eq. (5) enabled us to obtain the H_a and A values for paraelastic ($T > T_c$) and ferroelastic ($T < T_c$) phases (Table 1). The H_a and A values are seen to increase at the transition from the paraelastic to the ferroelastic phase. The temperature variation of the electric conductivity at the paraelastic-to-ferroelastic phase transition can be determined from the relation

$$\sigma T = A^p \exp\left(-\frac{H_a^p + \Delta\Phi_a}{kT}\right), \quad (7)$$

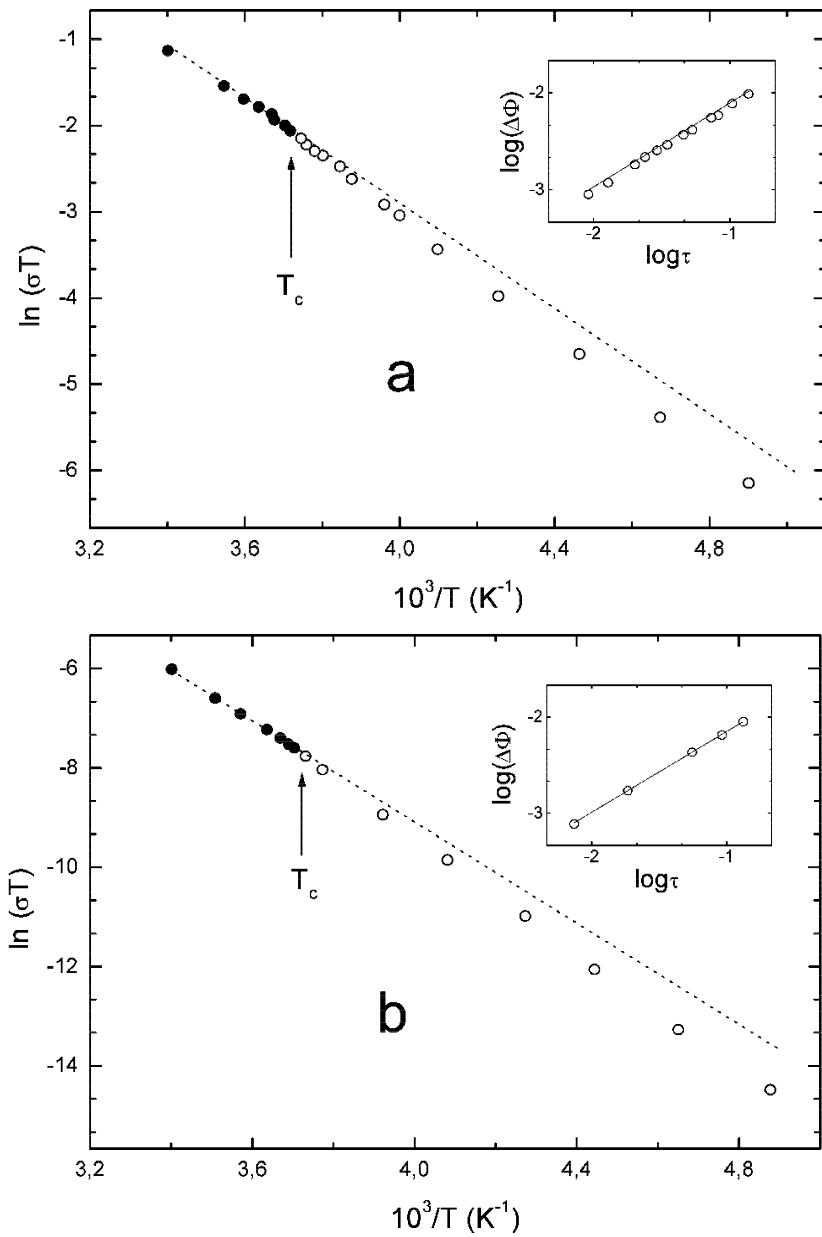


Fig. 3. Temperature dependence of $\ln(\sigma T) = f(10^3/T)$ for (a) $\text{Cu}_6\text{PS}_5\text{I}$ and (b) $\text{Cu}_6\text{PS}_5\text{Br}$ crystals, derived from the experimental values of the total electrical conductivity, presented in Ref. [11]. The inserts show the dependence $\log(\Delta\Phi_a) = f(\log \tau)$.

A^p and H_a^p being the values of the pre-exponential factor and the activation enthalpy in the paraelastic phase. At temperatures $T > T_c$, the increment of the thermodynamic potential is given by $\Delta\Phi_a = \Delta H_a - T\Delta S_a$, while at $T < T_c$, $\Delta\Phi_a$ increases following the relation

$$\Delta\Phi_a = \lambda\tau^\delta, \quad (8)$$

λ and δ being constants. Using the values of H_a^p and A^p for the paraelastic phase, the thermodynamic activation potential increment in the ferroelectric phase of $\text{Cu}_6\text{PS}_5\text{X}$ ($\text{X}=\text{Br},\text{I}$) crystals was calculated. The plots of $\log(\Delta\Phi_a) = f(\log\tau)$ (see the insert in Fig. 3) show the temperature dependences of $\Delta\Phi_a$ to be well approximated by a power function (8). Besides, they allow the determination of the power index δ , which, according to Ref. [12], is related to the critical index β of the PT order parameter ($\delta = 2\beta$). The obtained values of β_{el} and β_{opt} for the crystals under investigation differ from the classical (? Landau) value $\beta = 0.5$ (See Table 1). Finally, one should note that for the $\text{Cu}_6\text{PS}_5\text{Br}$ crystal, the values of β_{el} and β_{opt} are in good agreement with the value $\beta = 0.43$, obtained from the analysis of the temperature dependence of birefringence [4].

Finally, we note the importance of the correct choice of the fitting procedure for the determination of the critical indices. To determine the critical index β , a group of $\log(\Delta E_g^\alpha) = f(\log\tau)$ and $\log(\Delta\Phi_a) = f(\log\tau)$ plots were made by scaling T_c around the most probable value. From the dependences with the best linearity up to T_c , the T_c values were selected and the critical indices, listed in Table 1, were determined. For the $\text{Cu}_6\text{PS}_5\text{Br}$ crystal, the T_c value appeared to be the same for the $\log(\Delta E_g^\alpha) = f(\log\tau)$ and $\log(\Delta\Phi_a) = f(\log\tau)$ plots and equal to 270 K. As to the $\text{Cu}_6\text{PS}_5\text{I}$ crystal, the best fitting was obtained for $T_c = 272.5$ K for the $\log(\Delta\Phi_a) = f(\log\tau)$ plot and $T_c = 269$ K for the $\log(\Delta E_g^\alpha) = f(\log\tau)$ plot. Such difference in the T_c values can be explained by the difference of the growth conditions of the $\text{Cu}_6\text{PS}_5\text{I}$ samples, used for the isoabsorption studies and the electric measurements, since, as known from Ref. [13], the ferroelectric PT temperature can be varied within 10 K depending on the crystal growth procedures.

4. Conclusions

The results of the isoabsorption studies of $\text{Cu}_6\text{PS}_5\text{X}$ ($\text{X}=\text{Br}, \text{I}$) crystal optical absorption edge have shown that in the vicinity of the ferroelastic PT ($T = T_c$), a typical change (for the second-order PT) of the slope of the temperature dependence of the absorption edge energy position E_g^α is observed. A stepwise anomaly of the dependence of $E_g^\alpha(T)$, observed in the range of the first-order superionic PT, is smeared at the halogen substitution $\text{I} \rightarrow \text{Br}$. The analysis of the temperature dependences of total electric conductivity and $E_g^\alpha(T)$ has shown that the increments of ΔE_g^α and of thermodynamical potential of conductivity activation $\Delta\Phi_a$ are proportional to the square of the order parameter, and their variation at the ferroelastic PT can be described by the Landau theory.

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IZOAPSORPCIJSKA I ELEKTRIČNA ISTRAŽIVANJA KRISTALA Cu₆PS₅X
(X=Br, I) OKO FEROELASTIČNOG FAZNOG PRIJELAZA

Istražujem temperaturnu ovisnost položaja apsorpcijskog ruba E_g^α ($\alpha = 550 \text{ cm}^{-1}$) kristala Cu₆PS₅X (X=Br, I) u području temperature 77 do 323 K izoapsorpcijskim mjeranjima. Analiziram temperaturne promjene ukupne električne vodljivosti u području feroelastičnog faznog prijelaza drugog reda.