Optical absorption edge anomalies at superionic phase transition in Cu_6PSe_5Br crystals

I.P. Studenyak, Gy.Sh. Kovács, V.V. Panko, V.V. Mitrovcij, O.A. Mykajlo, V.O. Stefanovich

Institute of Solid State Physics and Chemistry, Uzhhorod National University, 46 Pidhirna St., 88000 Uzhhorod, Ukraine

Received 17.09.2001

Abstract

Temperature behaviour (77–320 K) of optical absorption edge in Cu_6PSe_5Br superionic crystals is studied. The spectral and temperature behaviour of the absorption edge is described by the Urbach rule. In the range of the first-order superionic phase transition the anomalous behaviour of the absorption edge parameters is revealed. The results of temperature isoabsorption studies are analyzed.

Keywords: Superionic conductor; phase transition; Urbach absorption edge.

PACS: 71.35.Cc; 78.40.Pg.

Introduction

Cu_6PSe_5Br crystals belong to the argyrodite family characterized by dense tetrahedral packing for phosphorus and sulphur atoms and partial population of systems of equivalent positions by copper atoms [1]. The latter results in the order-disorder type phenomena, phase transitions (PTs) and high ionic conductivity. Among the crystals of this family Cu_6PS_5X (X=Cl,Br,I) crystals, possessing both superionic and ferroelastic properties, are the most studied. At low temperatures in these crystals two PTs are realized, one of them being superionic (T_s), the other – ferroelastic (T_c) [2]. Optical absorption edge studies of Cu_6PS_5X (X=Cl,Br,I) crystals have shown that at low temperatures exciton absorption bands are revealed in the range of direct optical transitions [3]. With the temperature increase they are smeared, and at their long-wavelength tails exponential sections appear, being described by the Urbach rule [4, 5].

Very limited information about the crystals under investigation is available. At room temperature they, similarly to Cu_6PS_5Br crystals, belong to cubic syngony ($F\bar{4}3m$ space group) [1], and at low temperatures a superionic PT takes place at T_s=(259±1)K. The low-temperature phase symmetry at $T<T_s$ have not been determined unambiguously yet.

The present paper is aimed at the investigation of the temperature behaviour of Cu_6PSe_5Br crystal optical absorption edge parameters in the range of the superionic PT.

Experimental

Cu_6PSe_5Br single crystals were obtained by the chemical transport reaction method. The growth was carried out from the mixture, enriched with $CuBr+Cu_2Se$; copper monohalides being used as a transport agent.

Transmittance and reflectance measurements were performed for the samples, oriented

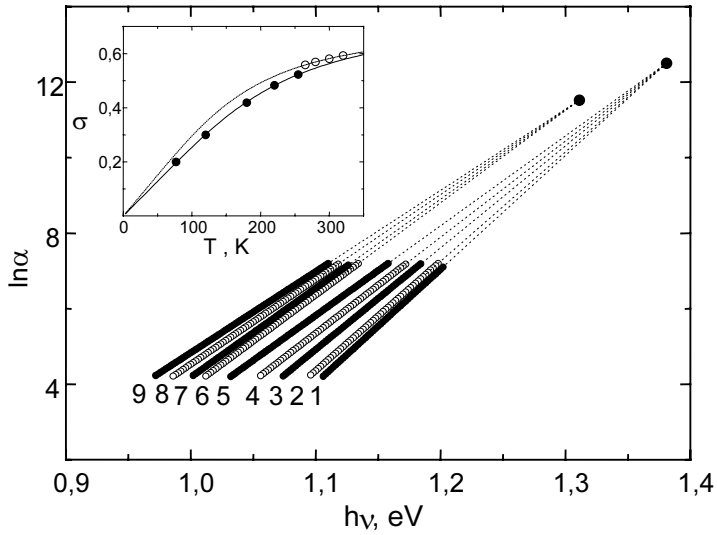

Fig.1. The spectral plots of the absorption coefficient logarithm for Cu_6PSe_5Br crystals at various temperatures *T*, K: 1 – 77, 2 – 120, 3 – 180, 4 – 220, 5 – 255, 6 – 265, 7 – 280, 8 – 300, 9 – 320. The insert depicts the temperature dependence of the $\sigma(T)$ parameter.

in the cubic phase, the incident light propagating along [100] crystallographic direction. The setup and technique for the absorption edge studies are descibed in [6]. Samples of various thickness (d≈20÷200 μm) were used for the studies, and the error in the absorption coefficient determination $\Delta\alpha/\alpha$ did not exceed 10%. The isoabsorption temperature studies consisted in the measurements of the absorption edge energy position at various temperatures and fixed absorbance values α.

Results and discussion

The results of the optical absorption edge studies for Cu_6PSe_5Br crystal at high absorption levels and in the temperature range 77–320 K are shown in Fig.1. Contrary to Cu_6PS_5Br [3], in Cu_6PSe_5Br crystals exciton bands at the absorption edge at low temperatures are not observed. At the absorption level $70\text{cm}^{-1} \le \alpha \le 1340\ \text{cm}^{-1}$ the absorption edge in the temperature range under investigation, including the non-superionic ($T<T_s$) and superionic ($T>T_s$) phases, has an exponential character and is described by the Urbach rule

$$\alpha(h\nu,T) = \alpha_0 \cdot \exp\left[\frac{h\nu - E_0}{w(T)}\right], \qquad (1)$$

where $w(T) = kT/\sigma(T)$ is the exponential absorption edge energy width. Contrary to Cu_6PS_5Br, in Cu_6PSe_5Br crystals for the superionic and non-superionic phases different focal convergency points for the Urbach absorption edge α_0 and E_0 are observed (See Table 1).

Table 1

Urbach absorption edge parameters of Cu_6PSe_5Br crystals

Temperature interval	$T<T_s$	$T>T_s$
$\alpha_0\,(\text{cm}^{-1})$	2.68×10^5	$1.01\cdot10^5$
E_0 (eV)	1.381	1.311
$\hbar\omega_p$ (meV)	0.0484	0.0395
θ_E (K)	562	458
σ_0	0.718	0.690
$E_g^*(0)$ (eV)	1.193	1.179
S_g	7.98	6.67
w_o (meV)	33.6	28.6
w_1 (meV)	69.0	57.1

The exponential shape of the long-wavelength absorption edge is known to be usually related to the electron-phonon interaction (EPI) effect [7]. The temperature behaviour of the $\sigma(T)$ parameter, characterizing the absorption edge slope, in the non-superionic ($T<T_s$) and superionic ($T>T_s$) phases is described by the known relation [8]

$$\sigma(T) = \sigma_0 \cdot \left(\frac{2kT}{\hbar\omega_p}\right) \cdot \tanh\left(\frac{\hbar\omega_p}{2kT}\right) \qquad (2)$$

and shown as an insert to Fig. 1. σ_0 parameter is constant within the same phase and is related to the EPI constant g as $\sigma_0=2/3g$, $\hbar\omega_p$ is the effective (mean) phonon energy in the single-oscillator model, describing the EPI [7]. The values of the EPI parameters σ_0 and $\hbar\omega_p$ are changed at the PT from the superionic phase to the non-superionic one (See Table 1). For Cu_6PSe_5Br crystals the value $\sigma_0<1$, what is the evidence for the strong EPI [7].

In Cu_6PSe_5Br crystals the direct band gap cannot be determined from the obtained absorption spectra, since the possible direct optical transitions are masked by the Urbach absorption tails. In such a case on the analysis of the absorption edge the optical pseudogap $E_g^*(T)$ value is used [6], corresponding to the absorption edge energy position at the absorption level $\alpha^*=10^3$ cm^{-1}:

$$E_g^*(T) = E_0 - \frac{kT}{\sigma(T)} \ln\left(\frac{\alpha_0}{\alpha^*}\right). \qquad (3)$$

The temperature dependences of the optical pseudogap E_g^* and the absorption edge energy width w of the crystals under investigation are given in Fig. 2. In the superionic PT range a stepwise change of E_g^* and anomalous behaviour of w are observed (Fig. 2).

The temperature variation of the energy gap E_g is known to be determined by two contributions: (i) lattice thermal expansion, and (ii) EPI [9]. For the crystals of this family the thermal expansion contribution is very small and can be neglected [6]. Since the EPI contribution is the most significant, the temperature variation of the optical pseudogap due to the EPI can be described by [10]

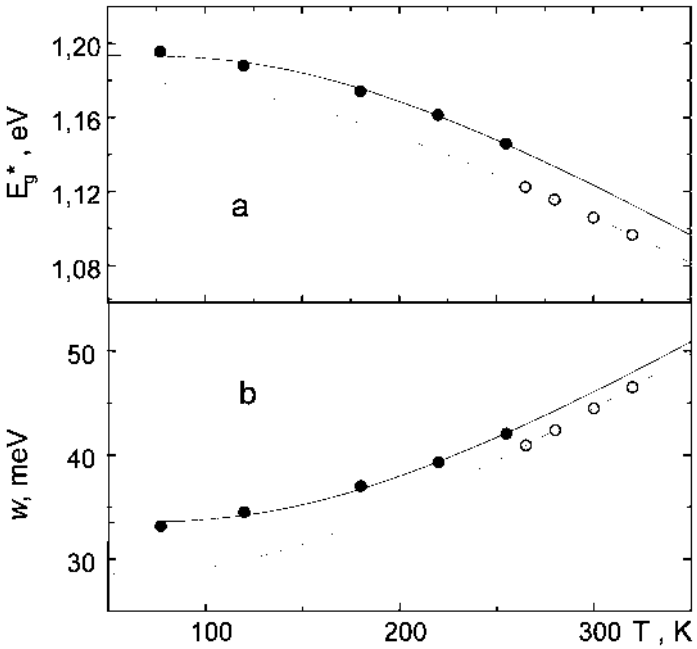

Fig. 2. The temperature dependences of the optical pseudogap E_g^* (a) and the Urbach absorption edge energy width w (b) for Cu_6PSe_5Br crystals.

$$E_g^*(T) = E_g^*(0) - S_g^* k\theta_E \left[\frac{1}{\exp(\theta_E / T) - 1} \right], \qquad (4)$$

where $E_g^*(0)$ is the energy gap at 0 K, S_g^* – a dimensionless constant of interaction, θ_E - the Einstein temperature, corresponding to the average phonon frequency of a system of non-interacting harmonic oscillators. The values of $E_g^*(0)$, S_g^* and θ_E for the non-superionic and the superionic phases, obtained from the calculations using Eq. (4), are listed in Table 1.

The temperature behaviour of the absorption edge energy width w in the Einstein model can be described as [11]

$$w(T) = w_0 + w_1 \left[\frac{1}{\exp(\theta_E / T) - 1} \right], \qquad (5)$$

where w_0 and w_1 are fitting parameters, independent of temperature within the same phase. The w_0 and w_1 values for the non-superionic and the superionic phases, obtained from the calculations using Eq. (5), are listed in Table 1.

The results of the detailed isoabsorption studies of the temperature behaviour of the absorption edge energy position E_g^α at the fixed absorption coefficient value α=520 cm^{-1} are shown in Fig. 3a. Based on the obtained dependence $E_g^\alpha(T)$ the temperature dependence of the variation ΔE_g^α was calculated (Fig.3b) at superionic-to-non-superionic PT as the increment of $E_g^\alpha(T)$ in the non-superionic phase with respect to the superionic one:

$$\Delta E_g^\alpha(T) = E_{g,n}^\alpha(T < T_s) - E_{g,s}^\alpha(T < T_s), \qquad (6)$$

where $E_{g,n}^\alpha(T < T_s)$ is the absorption edge energy position in the non-superionic phase, $E_{g,s}^\alpha(T < T_s)$ – the values, obtained by extrapolation (by means of Eq. (4)), of the experimental values for the superionic phase to the low-temperature range ($T<T_s$). Besides, in Fig. 3b the temperature dependence of $d(\Delta E_g^\alpha)/dT$ is presented, corresponding to the temperature behaviour of the anomalous part of the crystal specific heat. A sharp maximum in the temperature plot of $d(\Delta E_g^\alpha)/dT$ is seen to be observed in the first-order superionic PT range, from which the value of the superionic PT was determined: T_s= (258.9±0.5) K. As known from [12], the energy gap temperature variation (in our case ΔE_g^α) can be represented as an expansion over even powers of the PT order parameter η. Having restricted oneself by the first term of the expansion, one obtains:

$$\Delta E_g^* = a\eta^2 \ , \qquad (7)$$

a being the expansion coefficient. Thus, the temperature dependence of ΔE_g^α , shown in Fig. 3b, reproduces the temperature dependence of the PT order parameter square within the accuracy of the a coefficient.

According to the phenomenological theory, elaborated in [12] for the case of the Urbach behaviour, the ΔE_g^α variation in the range of the first-order PT is determined by the anomalies of three parameters of the Urbach rule α_0, E_0, σ (or w):

$$\Delta E_g^\alpha = \beta\eta^2 + \gamma\eta^2 + \ln(\alpha_0/\alpha)\delta\eta^2, \qquad (8)$$

where $\beta\eta^2$ is the contribution from the E_0 variation at the PT, $\gamma\eta^2$ – the contribution from the α_0 variation, $\ln(\alpha_0/\alpha)\delta\eta^2$ – the contribution from the σ variation. It follows from the obtained experimental results (Fig. 1) that in the crystals under investigation at $T = T_S$ all the three parameters of the Urbach relation (1) are changed. Since unambiguous determination of ΔE_g^α in the PT point from the experimental plot of E_g^α(T) is impossible due to the ambiguity of the choice of the PT temperature interval, it seemed interesting to calculate from Eq. (8) the "true" value of the stepwise change ΔE_g^α at

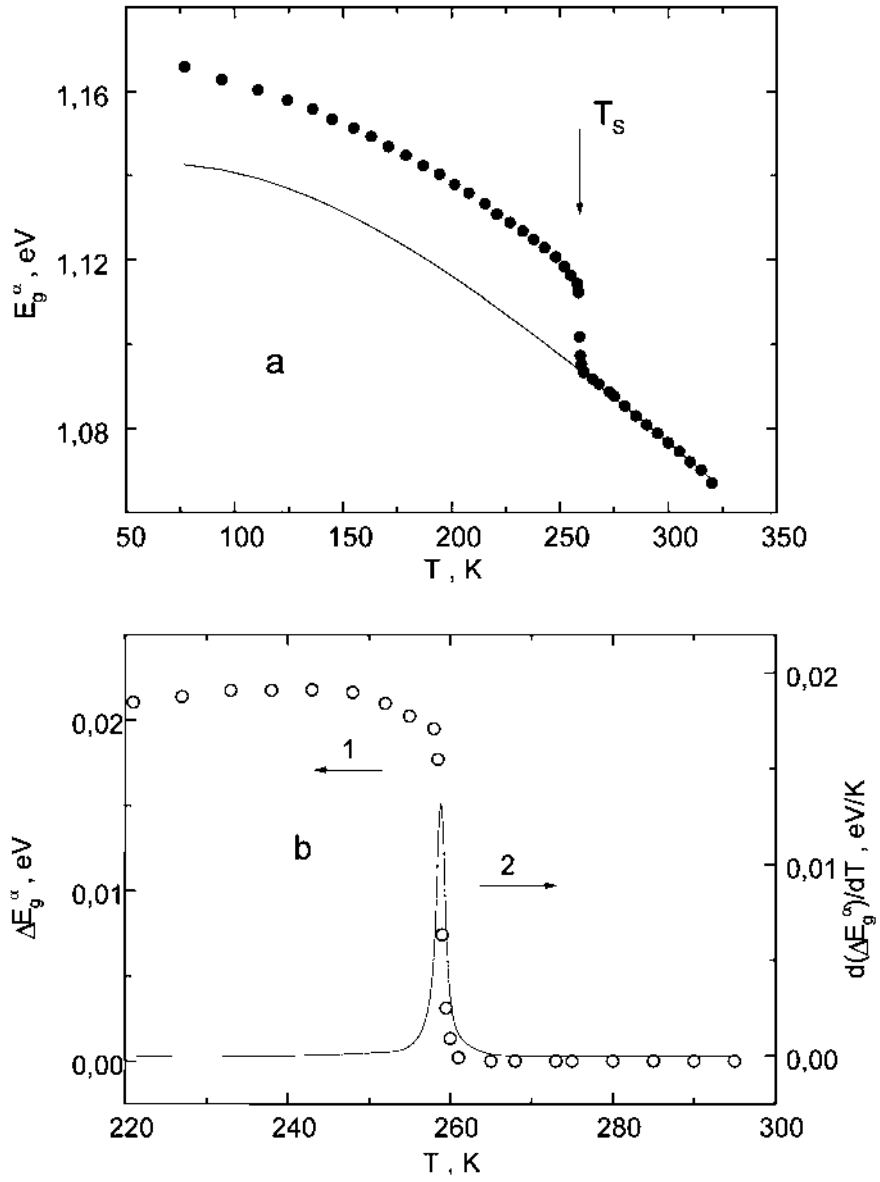

Fig.3. The temperature dependences of the absorption edge energy position E_g^α (a), its change ΔE_g^α (b, curve 1) and $d(\Delta E_g^\alpha)/dT$ (b, curve 2) for Cu_6PSe_5Br crystal

$T = T_S$. The calculated value of ΔE_g^α is 0.012 eV, being smaller than $\Delta E_g^\alpha \approx 0.019$ eV,obtained directly from the $E_g^\alpha(T)$ dependence.

Conclusions

The long-wavelength fundamental absorption edge of Cu_6PSe_5Br crystals in the non-superionic ($T < T_S$) and superionic ($T > T_S$) phases is of Urbach shape. In the superionic PT range the stepwise behaviour of the optical pseudogap E_g^* and the anomalous change of the absorption edge energy width w are observed. The obtained temperature dependence of ΔE_g^α reproduces the temperature dependence of the squared PT order parameter, and its temperature derivative – the temperature behaviour of the anomalous part of the specific heat of the investigated crystals.

References

1. Kuhs W.F., Nitsche R., Scheunemann K. Mater. Res. Bull. **14** (1979) 241.
2. Studenyak I.P., Stefanovich V.O., Kranjcec M., Desnica D.I., Azhniuk Yu.M., Kovacs Gy.Sh., Panko V.V. Solid State Ionics **95** (1997) 221.
3. Studenyak I.P., Kovacs Gy.S., Panko V.V., Kovacs E.T., Borets O.M. Fiz. Tverd. Tela **26** (1984) 2598
4. Studenyak I.P., Kovacs Gy.S., Orliukas A.S., Kovacs E.T. Izv. AN: Ser. Fiz. **56** (1992) 86 (in Russian).
5. Studenyak I.P., Kranjcec M., Kovacs Gy.S., Panko V.V., Azhnyuk Yu.M., Desnica D.I., Borets O.M., Voroshilov Yu.V. Materials Science and Engineering **B52** (1998) 202
6. Studenyak I.P., Kranjcec M., Kovacs Gy.S., Panko V.V., Desnica D.I., Slivka A.G., Guranich P.P. J. Phys. Chem. Sol. 60 (1999) 1897.
7. Kurik M.V. Phys. Stat. Sol. (a). **8** (1971) 9.
8. Sumi H., Sumi A. J. Phys. Soc. Japan. **56** (1987) 2211.
9. Allen P.B., Cardona M. Phys. Rev. B **23** (1981) 1495.
1. 10 Beaudoin M., G.DeVries A.J., Johnson S.R., Laman H., Tiedje T. Appl.Phys.Lett. **70** (1997) 3540.
10. Yang Z., Homewood K.P., Finney M.S., Harry M.A., Reeson K. J. Appl. Phys. **78** (1995) 1958.
11. Zametin V.I., Yakubovsky M.A., Rubkin L.M. Fiz. Tverd. Tela **21** (1979) 491(in Russian).