

Incommensurate Phase in Ferroelectrics: The Urbach Energy Remains Unchanged

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Abstract Temperature invariance of the Urbach energy and parallel red shift of optical absorption edge in the incommensurate phase of $\text{Sn}_2\text{P}_2\text{Se}_6$ ferroelectric is analyzed. The observed effect is explained by the presence of dynamic structural disordering of the crystal lattice caused by a wave of structure modulation which is formed by the shift of tin atoms.

Keywords Phase Transition, Incommensurate Phase, Absorption Edge

1. Introduction

It is well known that for a great number of solids absorption near the optical absorption edge increases exponentially and the spectral dependences of the absorption coefficient at different temperatures are described by the Urbach rule[1]. Since the discovery of this universal rule, it was set for a number of ferroics: ferroelectrics (e.g.[2-6]), ferrielectrics (e.g.[7,8]), antiferroelectrics (e.g.[9]), and ferroelastics (e.g.[10,11]). However, despite its versatility, in many cases deviations from this rule are observed. Some of these materials are ferroelectrics with incommensurate phase. The aim of this paper is an attempt to explain the non-Urbach behaviour of the optical absorption edge in incommensurate phases of some ferroelectrics from the standpoint of disordering processes and the presence of the dynamic component of structural disordering caused by the structure modulation. As an example, we have chosen $\text{Sn}_2\text{P}_2\text{Se}_6$ crystal which belongs to proper uniaxial ferroelectrics, in which at low temperatures two phase transitions exist, one of which is a phase transition from the paraelectric phase to the incommensurate phase at $T_i \approx 221$ K, the other is the phase transition from the incommensurate phase to the ferroelectric phase at $T_c = 193$ K[4, 5, 12].

2. Theory

In 1953, F. Urbach was the first to observe experimentally the exponential behaviour of absorption edge spectra in AgBr crystal, which formed a characteristic “bundle” at the

temperature increase[1]:

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

where E_U is the Urbach energy which is the value inverse to the absorption edge slope $E_U^{-1} = \Delta(\ln\alpha)/\Delta(h\nu)$; α_0 and E_0 are coordinates of the convergence point of the Urbach “bundle”. The temperature behaviour of the Urbach energy E_U in the framework of the Einstein model is described by the equation[13]

$$E_U = (E_U)_0 + (E_U)_1 \left[\frac{1}{\exp(\theta_E/T) - 1} \right] \quad (2)$$

where $(E_U)_0$ and $(E_U)_1$ are constants, θ_E is the Einstein temperature which corresponds to the average frequency of phonon excitations of non-interacting oscillators. It is known that the Urbach energy in solids is determined not only by temperature, but also by structural disordering[14]:

$$E_U(T, X) = K \left(\langle u^2 \rangle_T + \langle u^2 \rangle_X \right) \quad (3)$$

where K is a constant, $\langle u^2 \rangle_T$ and $\langle u^2 \rangle_X$ are mean-square deviations (displacements) of the atoms from their equilibrium positions, caused by the temperature disorder and the structural disorder of the solid-state system, respectively. As displacement of atoms from the equilibrium positions leads to a change in the electrical potential of the system, Eq. (3) can be written as

$$E_U = k_0 (W_T^2 + W_X^2) = (E_U)_T + (E_U)_X \quad (4)$$

where k_0 is a constant, W_T^2 and W_X^2 are mean-square deviations from the electric potential of a perfectly ordered structure, caused by the temperature and the structural disorder, respectively. The contributions of the temperature

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disordering $(E_U)_T$ and structural disordering $(E_U)_X$ to the Urbach energy E_U are considered independent, equivalent, and additive.

3. Experimental

$\text{Sn}_2\text{P}_2\text{Se}_6$ single crystals were obtained by chemical transport[15]. The studies were performed for the samples of different thickness $d=30\div 500$ μm in a broad temperature range 77–350 K. The incident light was linearly polarized, the electric field strength vector oscillating in planes parallel to X (coinciding with[100] crystallographic direction), or Y ([010] crystallographic direction). For transmission and reflection measurements a LOMO MDR-3 grating monochromator was used. The instrumental width was near 1 \AA . A UTREX cryostat was applied providing temperature stabilization within 0.1 K. The experimental setup and technique are described in Ref.[10].

4. Results and Discussion

The studies of optical absorption edge of $\text{Sn}_2\text{P}_2\text{Se}_6$ ferroelectric have revealed three typical temperature ranges: (i) the range of the Urbach behaviour of the absorption edge at $T < 193$ K, (ii) the range of parallel red shift of the optical absorption edge within the temperature interval $193 \leq T \leq 221$ K and (iii) the range of the Urbach behaviour of the absorption edge at $T > 221$ K (Fig. 1). The parallel red shift of the optical absorption edge in $\text{Sn}_2\text{P}_2\text{Se}_6$ and, consequently, the temperature invariance of the Urbach energy E_U (Fig. 2), like in the case of other materials with modulated structures such as $(\text{Pb}_y\text{Sn}_{1-y})_2\text{P}_2\text{Se}_6$ [16], CdP_2 , $\alpha\text{-ZnP}_2$ [17], $(\text{N}(\text{CH}_3)_4)_2\text{ZnCl}_4$ [18] $(\text{N}(\text{CH}_3)_4)_2\text{CuCl}_4$ [19], are related to the presence of the structure modulation in the incommensurate phase.

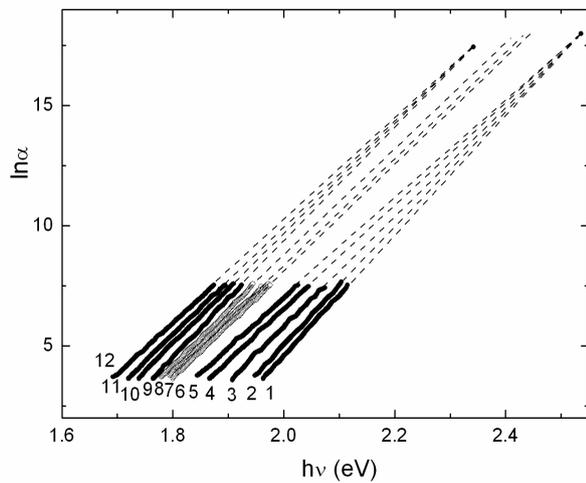


Figure 1. Spectral dependences of logarithm of absorption coefficient for $\text{Sn}_2\text{P}_2\text{Se}_6$ crystal at various temperatures T : 77 K (1), 110 K (2), 150 K (3), 180 K (4), 190 K (5), 195 K (6), 210 K (7), 220 K (8), 230 K (9), 270 K (10), 310 K (11), 350 K (12)

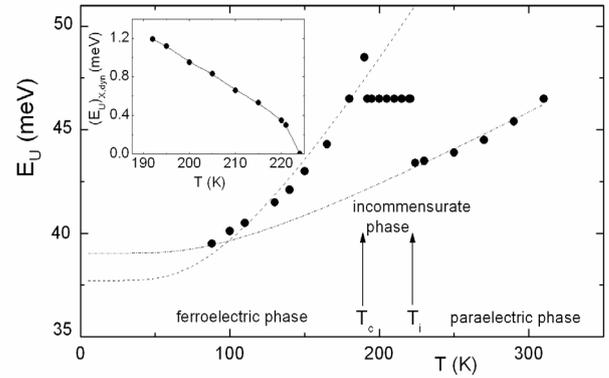


Figure 2. Temperature dependences of the Urbach energy E_U for $\text{Sn}_2\text{P}_2\text{Se}_6$ crystal. The insert shows the temperature dependence of the $(E_U)_{X,dyn}$ contribution

To explain the invariance of the Urbach energy E_U in the incommensurate phase (Fig. 2), we present the contribution of the structural disordering $(E_U)_X$ as a sum of two components – static structural disordering $(E_U)_{X,stat}$ and dynamic structural disordering $(E_U)_{X,dyn}$

$$E_U = (E_U)_T + (E_U)_{X,stat} + (E_U)_{X,dyn}, \quad (5)$$

thus the contribution of the temperature-independent static structural disordering $(E_U)_{X,stat}$ is caused by the presence of various defects, impurities and inhomogeneities of the crystal structure. Thus, in Ref.[20] it is shown that the most probable defects in $\text{Sn}_2\text{P}_2\text{Se}_6$ -type crystal lattice are the vacancies of Se atoms which result in the formation of deep levels in the band gap. The presence of the defects leads to the appearance of local non-uniform electrical fields which are revealed as the presence of a strong photorefractive effect and impurity-type photoconductivity[21, 22]. The contribution of the temperature-dependent dynamic structural disordering $(E_U)_{X,dyn}$ is caused by the presence of structure modulation in ferroics.

The values of these contributions were determined from Eq. (2), the parameters $(E_U)_0$, $(E_U)_1$ and Einstein temperature θ_E being obtained from the temperature dependence of the Urbach energy E_U . The calculations and further analysis showed that in the commensurate paraelectric ($T > T_i$) and ferroelectric ($T < T_c$) phases the temperature behaviour of E_U is determined by the temperature behaviour of the contribution $(E_U)_T$ caused by lattice thermal vibrations, at a constant value of $(E_U)_{X,stat} = \text{const}$ and in the absence of $(E_U)_{X,dyn} = 0$ (see Eq. (5)). In the incommensurate phase ($T_c < T < T_i$), with decreasing temperature the contribution of $(E_U)_T$ decreases; however, as the contribution $(E_U)_{X,dyn}$ increases and the contribution of $(E_U)_{X,stat}$ remains constant, the combination of these factors leads to the

temperature invariability of the Urbach energy $E_U = \text{const}$ (see Eq. (5), Fig. 2) and to the parallel red shift of the absorption edge (Fig. 1). Dynamic structural disordering $(E_U)_{X, \text{dyn}}$ in the incommensurate phase is caused by the appearance of a modulation wave formed by displacement of tin atoms in (010) symmetry plane along a direction close to [100] (See Ref.[23]). With the temperature variation, the changes of the amplitude and the period of the modulation wave are observed whereas the direction of the modulation wave vector remains unchanged[23].

Thus, the temperature range for which the condition $(E_U)_{X, \text{dyn}} \neq 0$ becomes true and the parallel red shift of the optical absorption edge as well the temperature invariance of the Urbach energy E_U are observed, can be identified as the range of existence of the incommensurate phase in ferroics. The observed features of the absorption edge behaviour in the incommensurate phase of $\text{Sn}_2\text{P}_2\text{Se}_6$ crystal are characteristic properties of incommensurate superstructures, similarly to the invar effect[24] and anomalous hysteresis[25].

5. Conclusions

In $\text{Sn}_2\text{P}_2\text{Se}_6$ ferroelectric, the dynamic structural disordering of the crystal lattice, the parallel red shift of optical absorption edge and the temperature invariance of Urbach energy are observed in the incommensurate phase in the temperature range $193 \leq T \leq 221$ K. The presence of the dynamic structural disordering $(E_U)_{X, \text{dyn}}$ in the incommensurate phase of $\text{Sn}_2\text{P}_2\text{Se}_6$ is caused by modulation wave, the parameters of which depend on temperature.

REFERENCES

- [1] F. Urbach, "The long-wavelength edge of photographic sensitivity and electronic absorption of solids", *APS Journals, Phys. Rev.*, vol.92, pp.1324-1326, 1953
- [2] V.I. Zametin, M.A. Yakubovskii, L.M. Rabkin, "Anomalies of absorption edge at phase transitions", *Maik, Fiz. Tverd. Tela*, vol.21, no.2, pp.491-498, 1979[English translation: *Maik, Sov. Phys. Solid State*, vol.21, pp. 291-298, 1979].
- [3] K. Zickus, A. Audzijonis, J. Batarunas, A. Sileika, "The fundamental absorption edge tail of ferroelectric SbSI ", *Wiley-VCH, Phys. Stat. Sol.(b)*, vol.125, no.2, pp.645-651, 1984.
- [4] P.P. Guranich, E.I. Gerzanich, A.G. Slivka, V.S. Shusta, V.A. Bobela, "Phase p,T,x-diagram and peculiarities of physical properties of $(\text{Pb}_x\text{Sn}_{1-x})_2\text{P}_2\text{Se}_6$ crystals with an incommensurate phase", *Taylor & Francis, Ferroelectrics*, vol.132, pp.173-183, 1992.
- [5] V.S. Shusta, E.I. Gerzanich, A.G. Slivka, P.P. Guranich, V.A. Bobela, "Phase transitions and physical properties of $(\text{Pb}_y\text{Sn}_{1-y})_2\text{P}_2\text{Se}_6$ crystals at high hydrostatic pressures", *Taylor & Francis, Ferroelectrics*, vol.145, pp. 61-71, 1993.
- [6] K. Noba, Y. Kayanuma, "Urbach tail for ferroelectric materials with an order-disorder-type phase transition", *Phys. Rev. B, APS Journals*, vol.60, no.7, pp.4418-4421, 1999.
- [7] I.P. Studenyak, V.V. Mitrovicij, Gy.Sh. Kovacs, M.I. Gurzan, O.A. Mykajlo, Yu.M. Vysochanskii, V.B. Cajipe, "Disordering effect on optical absorption processes in CuInP_2S_6 layered ferroelectrics", *Wiley-VCH, Phys. Stat. Sol.(b)*, vol.236, no.3, pp.678-686, 2003.
- [8] I.P. Studenyak, O.A. Mykajlo, V.O. Stephanovich, M.I. Gurzan, Yu.M. Vysochanskii, V.B. Cajipe, "Phase transitions and optical absorption edge in CuInP_2S_6 layered ferroelectrics", *Wiley-VCH, Phys. Stat. Sol.(a)*, vol.198, no.2, pp. 487-494, 2003.
- [9] I.P. Studenyak, O.A. Mykajlo, Yu.M. Vysochanskii, V.B. Cajipe, "Optical absorption studies of phase transitions in CuCrP_2S_6 layered antiferroelectrics", *IOP Publishing, J. Phys.: Condens. Matter.*, vol.15, pp.6773-6779, 2003.
- [10] I.P. Studenyak, M. Kranjčec, Gy.Sh. Kovacs, I.D. Desnica, V.V. Panko, Slivka V.Yu., "Influence of compositional disorder on optical absorption processes in $\text{Cu}_6\text{P}(\text{S}_{1-x}\text{Se}_x)_5\text{I}$ crystals", *MRS, J. Mater. Res.*, vol.16, no.6, pp.1600-1608, 2001.
- [11] I.P. Studenyak, M. Kranjčec, M.V. Kurik, "Urbach rule and disordering processes in $\text{Cu}_6\text{P}(\text{S}_{1-x}\text{Se}_x)_5\text{Br}_{1-y}\text{I}_y$ superionic conductors", *Elsevier, J. Phys. Chem. Solids*, vol.67, pp.807-817, 2006.
- [12] A.G. Slivka, E.I. Gerzanich, V.S. Shusta, P.P. Guranich, "Influence of isomorphic substitution and external hydrostatic pressure on fundamental absorption edge in $\text{Sn}(\text{Pb})_2\text{P}_2\text{S}(\text{Se})_6$ crystals", *Maik, Izv. Vuzov: Ser. Physics*, vol.9, pp. 23-28, 1999.
- [13] Z. Yang, K.P. Homewood, M.S. Finney, M.A. Harry, K.J. Reeson, "Optical absorption study of ion beam synthesized polycrystalline semiconducting FeSi_2 ", *AIP, J. Appl. Phys.*, vol.78, no.3, pp. 1958-1963, 1995.
- [14] G.D. Cody, T. Tiedje, B. Abeles, B. Brooks, Y. Goldstein, "Disorder and the optical-absorption edge of hydrogenated amorphous silicon", *APS Journals, Phys. Rev. Lett.*, vol.47, no.20, pp. 1480-1483, 1981.
- [15] C. Carpentier, R. Nitsche, "Vapour growth and crystal data of thio(seleno)-hipodiphosphates and their mixed crystals", *Elsevier, Mat. Res. Bull.*, vol.9, pp. 401-410, 1974.
- [16] P.P. Guranich, E.I. Gerzanich, A.G. Slivka, V.S. Shusta, "Absorption edge in $(\text{Pb}_x\text{Sn}_{1-x})_2\text{P}_2\text{Se}_6$ ferroelectric crystals with incommensurate phase", *Nauka, Ukr. Fiz. Zhurnal*, vol.35, no.4, pp.196-199, 1990.
- [17] V.A. Zuyev, N.Yu. Lavriyenko, A.A. Melnikov, V.G. Fedotov, "Peculiarities of absorption edge in $\alpha\text{-ZnP}_2$ ", *Nauka, Ukr. Fiz. Zhurnal*, vol.35, no.3, pp.346-349, 1990.
- [18] O.G. Vlokh, I.I. Polovynko, and S.A.Sveleba, "Optical absorption in incommensurate $(\text{N}(\text{CH}_3)_4)_2\text{ZnCl}_4$ crystals", *Nauka, Ukr. Fiz. Zhurnal*, vol.35, no.1, pp.49-52, 1990.
- [19] O.G. Vlokh, I.I. Polovynko, S.A.Sveleba, "Optical absorption in incommensurate $(\text{N}(\text{CH}_3)_4)_2\text{CuCl}_4$ crystals", *Maik, Optika i Spektroskopiya*, vol.65, no.6, pp.1272-1275, 1988.
- [20] Yu.M. Vysochanskii, V.Yu. Slivka, "Ferroelectrics of $\text{Sn}_2\text{P}_2\text{S}_6$ family. Properties in vicinity of Lifshits point, Vyscha Shkola,

Ukraine, 1994.

- [21] S.G. Odoulov, A.N. Shumelyuk, U. Hellwig, R.A. Rupp, A.A. Grabar, I.M. Stoyka, "Protorefraction in tin hypophosphite in near infrared", *APS Journals, J. Opt. Soc. Am. B*, vol.13, no.10, pp.2352-2360, 1996.
- [22] A.A. Grabar, "Light-induced electric conductivity in $\text{Sn}_2\text{P}_2\text{S}_6$ ", Taylor & Francis, *Ferroelectrics*, vol. 192, pp. 155-159, 1997.
- [23] T.K. Parsamyan, S.S. Khasanov, and V.Sh. Shekhtman, Yu.M. Vysochanskii, V.Yu. Slivka, "Incommensurate phase in proper $\text{Sn}_2\text{P}_2\text{Se}_6$ ferroelectric", *Maik, Fiz. Tverd. Tela*, vol.27, pp. 3327-3331, 1985[English translation: *Maik, Sov. Phys. Solid State*, vol.27, pp. 2003-2007, 1985].
- [24] T.K. Parsamyan, S.S. Khasanov, V.Sh. Shekhtman, "Invar effect in crystals of quasibinary system with Lifshits point", *Maik, Fiz. Tverd. Tela*, vol.29, pp. 1665-1668, 1987[English translation: *Maik, Sov. Phys. Solid State* vol.29, pp. 958-961, 1987].
- [25] B.A. Strukov, I. Uezu, V.M. Arutyunova, "Anomalous temperature and dielectrical hysteresis at phase transition from incommensurate to commensurate polar phase in $(\text{NH}_4)_2\text{BeF}_4$ crystals", *Maik, Pisma Zh. Eksper. Teor. Fiz.*, vol.35, pp.424-427, 1982.