Optical absorption studies of phase transitions in CuCrP$_2$S$_6$ layered antiferroelectrics

# Optical absorption studies of phase transitions in CuCrP$_2$S$_6$ layered antiferroelectrics

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**Abstract**
The temperature behaviour of the optical absorption edge in the range of phase transitions for CuCrP$_2$S$_6$ crystals is studied. The absorption edge is shown to be described by the Urbach rule with different convergence point coordinates in antiferroelectric and paraelectric phases. In the intermediate phase there is no convergence point and a parallel shift of the exponential absorption edge is observed. The specific features of the temperature behaviour of the absorption edge are treated assuming the intermediate phase in CuCrP$_2$S$_6$ crystals to be an incommensurate one.

## 1. Introduction

CuCrP$_2$S$_6$ crystals belong to layered two-dimensional structures of the CuMP$_2$S$_6$ (M = Cr, In) type [1–4]. They are formed by layers built up by cores of sulfur atoms where metal cations and P–P pairs fill octahedral voids. Cu$^+$ ions can occupy two positions, whose population varies with temperature: off-centre (displaced from the centres of the octahedra) Cu1 and close to central Cu2 positions. In turn, two types of positions for Cu1 are distinguished: Cu1$^u$, displaced 'upward' from the middle of the layer (the centres of the octahedra), and Cu1$^d$, displaced 'downward' from the middle of the layer.

According to calorimetric, dielectric and x-ray data [3], CuCrP$_2$S$_6$ crystals undergo two phase transitions (PTs), at $T_{c1} \approx 190$ K and $T_{c2} \approx 150$ K, and separate into three phases: paraelectric [1, 3] $(T > T_{c1})$, antiferroelectric [2] $(T < T_{c2})$ and intermediate quasi-antipolar in the temperature range $T_{c2} < T < T_{c1}$ [4]. X-ray studies have shown the paraelectric phase to have $C2/c$ symmetry and the antiferroelectric phase $Pc$ symmetry [3]. Cu$^+$ ions at $T > T_{c1}$ are distributed equally among different positions and in the intermediate phase 'freeze' with the 'upward' Cu1$^u$ and 'downward' Cu1$^d$ positions having a population ratio of 71%:29%. The intermediate phase in CuCrP$_2$S$_6$ crystals is characterized by incomplete antipolar ordering of the copper atom sublattice and is treated as a kind of dipolar glass [3, 4]. At $T < T_{c2}$ Cu$^+$

ion hopping is 'frozen' in one of the off-centre positions, resulting in the appearance of static dipoles and antipolar ordering in the copper sublattice. Besides the above PTs, in $CuCrP_2S_6$ crystals an antiferromagnetic structure of magnetic $Cr^{3+}$ ions is revealed at $T < T_N \approx 30$ K [3, 5].

The present paper is aimed at studying the PT, disordering processes and the nature of the intermediate phase by temperature investigations of optical absorption edge.

## 2. Experimental details

$CuCrP_2S_6$ crystals were obtained by chemical transport reactions [1]. Absorption edge studies were carried out for samples of different thickness ($d = 60$–150 $\mu$m) in the temperature range 77–325 K. The light beam was propagated along the normal to the layer plane. The incident light was linearly polarized, the electric field strength vector oscillating in the plane parallel to the crystallographic axis $Y$ ($E \parallel Y$). A crystallographic notation was used [6] where the $Y$ axis in crystals with monoclinic syngony coincides with the second-order axis (for the paraelectric phase space group $C2/c$) or with a normal to the symmetry plane (for the antiferroelectric phase space group $Pc$). An MDR-3 diffraction monochromator was used for transmittance and reflectance measurements. The spectral slit was about 1 Å. A UTREX cryostat was used, the temperature being stabilized within 0.1 K. The linear absorption coefficient $\alpha$ as a function of transmittance $T$ and reflection of the surface $R$ were calculated using the following well known formula, which takes into account multiple internal reflections [7]:

$$\alpha = \frac{1}{d} \ln \left[ \frac{(1-R)^2}{2T} + \sqrt{\left( \frac{(1-R)^2}{2T} \right)^2 + R^2} \right] \qquad (1)$$

where $d$ denotes the plane-parallel sample thickness. The relative error in the absorbance measurements $\Delta\alpha/\alpha$ does not exceed 10% at $0.3 \leqslant \alpha d \leqslant 3$ [8].

## 3. Results and discussion

Optical absorption edge spectra of $CuCrP_2S_6$ crystals, obtained in the temperature range 77–325 K, are shown in figure 1. Contrary to $CuInP_2Se_6$ [9] and $CuInP_2S_6$ [10] crystals, where at low temperatures direct allowed optical transitions and exciton absorption bands, respectively, are observed, in $CuCrP_2S_6$ crystals the absorption edge in the temperature interval under investigation has an exponential shape and is described by the empirical Urbach law [11]:

$$\alpha(h\nu) = \alpha_0 \exp\left( \frac{h\nu - E_0}{w} \right) \qquad (2)$$

where $w$ is the energy width of the exponential absorption edge and $\alpha_0$ and $E_0$ are empirical parameters. The convergence point coordinates $\alpha_0$ and $E_0$ of the exponential sections of the Urbach absorption edge are shown to differ for antiferroelectric ($T < T_{c2}$) and paraelectric ($T > T_{c1}$) phases (table 1). In the intermediate phase ($T_{c2} < T < T_{c1}$) there is no convergence point, and parallel shift of the exponential absorption edge is observed. The temperature dependences of the energy width of the absorption edge, $w$, for antiferroelectric and paraelectric phases in the Einstein model can be described by the relationship [12]

$$w = w_0 + w_1 \left( \frac{1}{\exp(\theta_E/T) - 1} \right) \qquad (3)$$

where $w_0$ and $w_1$ are constant values within the same phase and $\theta_E$ is the Einstein temperature corresponding to the mean frequency of phonon excitations. The parameter values of $w_0$ and
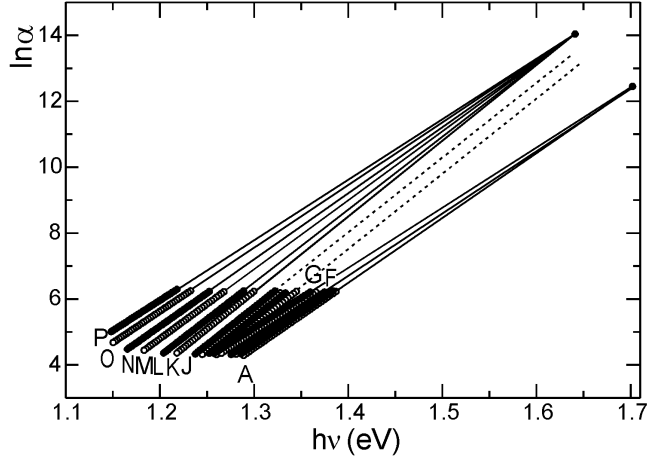
**Figure 1.** Spectral dependences of the logarithm of absorbance for CuCrP$_2$S$_6$ crystal at various temperatures (in K): A, 77; B, 90; C, 100; D, 115; E, 130; F, 140; G, 150; H, 160; I, 170; J, 180; K, 205; L, 225; M, 250; N, 273; O, 300; P, 325.

**Table 1.** The energy position of the absorption edge, $E_g^\alpha$ ($\alpha = 800$ cm$^{-1}$), and the energy width of the absorption edge, $w$, at $T = 325$ K; $\alpha_0$ and $E_0$ are the Urbach absorption edge parameters. EPI parameters $\hbar\omega_p$ and $\sigma_0$ as well as $\theta_E$, $w_0$ and $w_1$, obtained while describing the experimental results by equations (2)–(4) for CuInP$_2$S$_6$ [9] and CuCrP$_2$S$_6$ crystals, are also shown.

| Crystal | CuInP$_2$S$_6$ | CuCrP$_2$S$_6$ | |
|---|---|---|---|
| $E_g^\alpha$ (eV) | 2.623 | 1.239[a] | |
| $w$ (meV) | 107.5 | 55.2 | |
| Temperature interval (K) | 315–573 | 77–150 | 190–273 |
| $\alpha_0$ (cm$^{-1}$) | $1.66 \times 10^5$ | $2.55 \times 10^5$ | $1.25 \times 10^6$ |
| $E_0$ (eV) | 3.195 | 1.702 | 1.641 |
| $\sigma_0$ | 0.269 | 0.380 | 0.625 |
| $\hbar\omega_p$ (meV) | 17.5 | 38.4 | 47.7 |
| $\theta_E$ (K) | 203 | 446 | 554 |
| $w_0$ (meV) | 32.3 | 50.6 | 38.3 |
| $w_1$ (meV) | 65.1 | 104.2 | 76.3 |

[a] For CuCrP$_2$S$_6$ crystal the $E_g^\alpha$ value at $\alpha = 800$ cm$^{-1}$ is determined by linear extrapolation of $\ln\alpha(h\nu)$ plot to the high absorption level range.

$w_1$, obtained while describing the experimental temperature dependence of $w$ (figure 2) by equation (3), are listed in table 1.

In the vicinity of the PT the changes in the temperature dependence of the energy width of the absorption edge, $w$, are observed; in the range of the intermediate phase it is independent of temperature. In figure 2 the temperature behaviour of the parameter $\sigma = kT/w$ is also shown, which in the antiferroelectric and paraelectric phases is described by the known formula [13]

$$\sigma(T) = \sigma_0 \left( \frac{2kT}{\hbar\omega_p} \right) \text{th} \left( \frac{\hbar\omega_p}{2kT} \right), \tag{4}$$

where $\hbar\omega_p$ is the effective phonon energy in the single-oscillator model describing the electron–phonon interaction (EPI), $\sigma_0$ is a parameter related to the EPI constant $g$ as $\sigma_0 = 2/3g$ [13] and th is the hyperbolic tangent function. The values obtained for $\hbar\omega_p$ and $\sigma_0$ are listed in table 1. In CuCrP$_2$S$_6$ crystals $\sigma_0 < 1$; this is evidence for strong EPI [14].
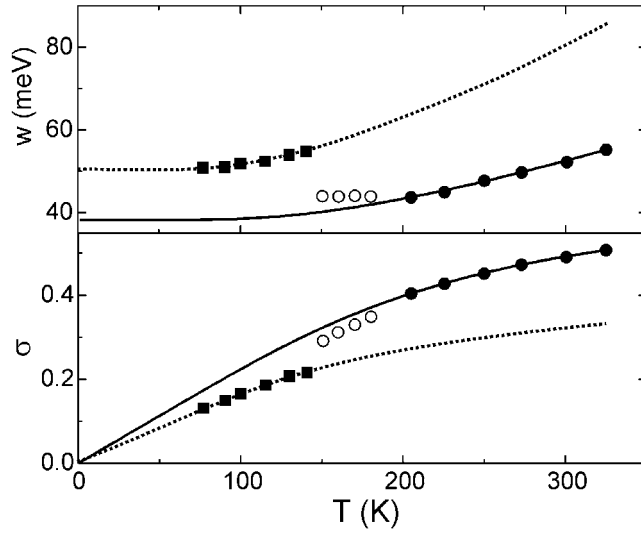
**Figure 2.** Temperature dependences of the characteristics of the exponential absorption edge of CuCrP$_2$S$_6$ crystal: the energy width $w$ and the parameter $\sigma = kT/w$. The experimental values for $T < T_{c2}$ are presented by full squares, for $T_{c2} < T < T_{c1}$—by open circles, and for $T > T_{c1}$—by full circles. The calculated dependences, obtained by using equations (3) and (4), for $T < T_{c2}$ are shown by dotted curves, and for $T > T_{c1}$ by full curves.

It is important to note that no convergence of $\ln \alpha(h\nu)$ dependences is observed in the whole intermediate phase interval $T_{c2} < T < T_{c1}$. One possible reason for this may lie in the presence of modulation of the spatial distribution of spontaneous polarization. Such modulation results in a change in the wavevector selection rules which is to some extent similar to the manifestation of disordering typical for glasses. At $T < T_{c2}$ the structure modulation disappears, and a convergence point exists again. One more interesting feature of the intermediate phase is the fact that the energy width of the absorption edge, $w$, is independent of temperature (i.e. $w = $ constant). In accordance with equation (3), this is possible in the case when $(\theta_E/T) = $ constant. Hence the temperature dependence of $\theta_E(T)$ or the 'effective' (average) phonon frequency $\omega_p = k\theta_E/\hbar$ follows. If the average phonon frequency in the paraelectric phase is denoted as $\omega_{p,p}$, its temperature dependence in the intermediate incommensurate phase can be given by

$$\omega_{p,i}(T) = \omega_{p,p} - \Delta\omega_p(T) \tag{5}$$

where $\Delta\omega_p(T)$ characterizes the variation of the phonon spectrum due to the structure modulation. The calculations show $\Delta\omega_p$ to grow linearly with the decrease in temperature in the intermediate phase of CuCrP$_2$S$_6$ (figure 3).

Since for CuCrP$_2$S$_6$ crystals direct allowed transitions are masked by the exponential absorption 'tails', the direct energy gap cannot be determined. Therefore, in order to describe the temperature shift of the absorption edge we had to use the so-called energy position of the absorption edge, $E_g^\alpha$, being determined at a fixed value of absorbance $\alpha = 400 \, \text{cm}^{-1}$ (figure 4). It should be noted that the temperature variation of $E_g^\alpha$ can be described by the relationship [15]

$$E_g^\alpha(T) = E_g^\alpha(0) - S_g^\alpha k\theta_E \left[ \frac{1}{\exp(\theta_E/T) - 1} \right) \tag{6}$$

where $E_g^\alpha(0)$ is the energy gap at 0 K and $S_g^\alpha$ is a constant. The performed calculations have shown that in the antiferroelectric and paraelectric phases the experimental values of $E_g^\alpha$ are
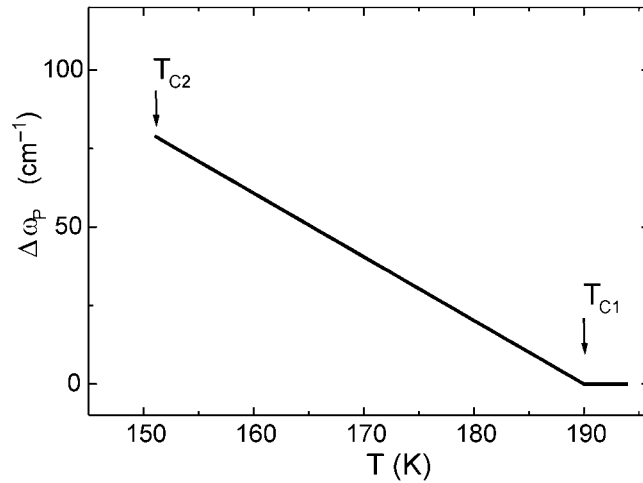
**Figure 3.** Temperature dependence of 'effective' frequency variation $\Delta\omega_p$ for CuCrP$_2$S$_6$ crystal in the intermediate phase range.
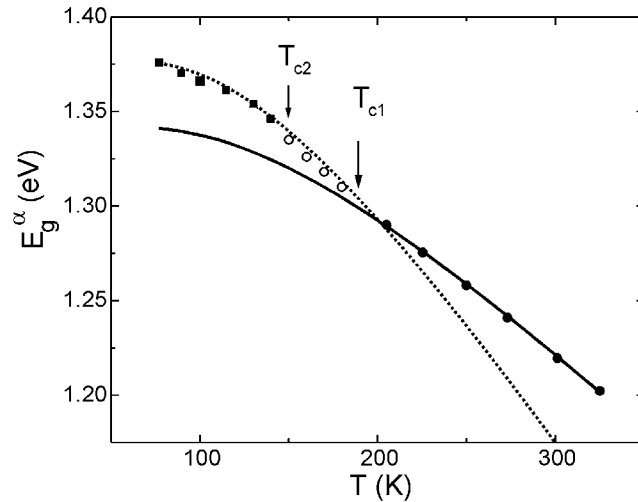


**Figure 4.** Temperature dependence of the energy position of the absorption edge $E_g^\alpha$ ($\alpha = 400$ cm$^{-1}$), obtained in the heating mode. The plots, calculated in accordance with equation (6), are presented by dotted and full curves: for $T < T_{c2}$ the energy gap at $T = 0$ K is $E_g^\alpha(0) = 1.376$ eV, a dimensionless constant $S_g^\alpha = 18.0$; for $T > T_{c1}$, $E_g^\alpha(0) = 1.33$ eV and $S_g^\alpha = 12.2$.

well described by equation (6). The temperature dependence of $E_g^\alpha$ shows a well-smeared step in the first-order PT range at $T_{c2} \approx 150$ K and a change in the slope of the temperature dependence in the second-order PT range at $T_{c1} \approx 190$ K (figure 4).

Now we consider the temperature behaviour of the absorption edge using the x-ray data [3] and in view of the disordering processes taking place in the CuCrP$_2$S$_6$ crystal structure. Temperature dependences of $E_g$ and $w$ are known to reflect the influence of various types of disordering upon the optical absorption edge: temperature (quasiharmonic thermal vibrations of atoms) and structural (dynamic and static) disordering [16]. In the antiferroelectric phase

the copper sublattice in $CuCrP_2S_6$ crystals is the result of complete alternating occupation of 'upward' $Cu1^u$ and 'downward' $Cu1^d$ sites. Copper atoms form an ordered structure of oppositely directed dipoles with zero total polarization. Being located in the mentioned sites, copper atoms perform almost harmonic vibrations. Hence, the temperature behaviour of the Urbach absorption edge in this phase is determined by the temperature disordering due to the thermal vibrations of the lattice atoms and the static structural disordering due to various kinds of defect. In the intermediate phase the extent of occupation of Cu1 sites is changed, which results in the redistribution of probabilities for copper atoms to be located in $Cu1^u$ and $Cu1^d$ sites in each elementary unit. As a result, in the neighbouring cells such an extent of site occupation is realized alternately: for example, 59% $Cu1^u$ and 41% $Cu1^{d'}$; 79% $Cu1^d$ and 21% $Cu1^{u'}$. Such quasi-antipolarity of the copper sublattice in the intermediate phase is the result of the structure modulation typical of incommensurate phases. In the paraelectric phase the occupation is the same for all elementary units, and here gradual occupation of Cu2 sites takes place. Cu1–Cu2 hopping results in dynamic structural disordering in the copper cation sublattice. Besides, the hopping motion is the reason for ionic conductivity [17].

While comparing the absorption edge for $CuInP_2S_6$ and $CuCrP_2S_6$ crystals (see table 1), In → Cr substitution is noted to result in a considerable decrease of the energy gap $E_g^\alpha$ (~1.38 eV) and the energy width of the absorption edge, $w$, (~52 meV). Contrary to $CuInP_2S_6$ [9], where the Urbach shape of the absorption edge is observed only in the paraelectric phase (as already mentioned, the ferrielectric phase is characterized by direct optical transitions), in $CuCrP_2S_6$ the Urbach edge is observed in both antiferroelectric and paraelectric phases, the coordinates of the convergence point being different. In → Cr substitution results in weakening of the EPI ($\sigma_0$ increase) and the increase of the effective phonon energy $\hbar\omega_p$. A value of $w$ almost two times higher in the paraelectric phase of $CuInP_2S_6$ crystal is probably related to the fact that here additional disordering occurs due to the hopping motion of $Cu^+$ ions from Cu1 to Cu3 sites, which are placed in an interlayer space [18].

## 4. Conclusions

In the antiferroelectric $(T < T_{c2})$ and paraelectric $(T > T_{c1})$ phases the absorption edge in $CuCrP_2S_6$ crystal possesses an exponential Urbach shape. In the intermediate $(T_{c2} < T < T_{c1})$ phase there is no convergence point, a parallel shift of the exponential absorption edge occurs and the energy width of the absorption edge is independent of temperature. The characteristic features of the temperature behaviour of optical absorption enable us to assume the intermediate phase in $CuCrP_2S_6$ to be an incommensurate phase. In the range of the PT the parameters of the Urbach absorption edge are changed, this variation being determined by the specific features of the EPI and the effect of various types of disordering: temperature disordering (due to the lattice thermal vibrations) and static structural disordering in the antiferroelectric phase, and temperature, static and dynamic structural disordering in the paraelectric phase. As follows from the comparison of the optical absorption spectra of $CuInP_2S_6$ and $CuCrP_2S_6$ crystals, In → Cr cation substitution leads to the decrease of the energy gap and the energy width of the edge, to weakening of the EPI and to an increase in the effective phonon energy $\hbar\omega_p$.

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