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# Band structure and optical constants of $SnS_2$ single crystals

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**Annotation:** Absorption (***K***), reflection (***R***) and wavelength modulated transmission ($\Delta T/\Delta\lambda$) spectra in $SnS_2$ crystals of hexagonal phase (space group ***P6₃/mmc***) were investigated in temperature interval from 300 to 10 K. It was established that indirect band gap ($E_g^{ind}$ - 2.403 eV) is due to unpolarized indirect transitions between Γ and M points of Brillouin zone. A minimal direct band gap ($E_g^{dir}$ - 2.623 eV) in E||b polarization is formed by direct allowed transitions and in E⊥b polarization (2.698 eV) by forbidden transitions in Γ point of Brillouin zone. A magnitude of refractive index (***n***) changes from 3 to 4 and has a maximum at 2.6 eV. Optical functions (***n***, ***k***, $\varepsilon_1$ and $\varepsilon_2$) in energy region $E > E_g$ (3 - 6.5 eV) were calculated from measured reflection spectra by Kramers-Kronig analysis. Features observed in reflection and optical function spectra were assigned to electron transitions. This electron transitions were localized in framework of theoretically calculated band structure.

Keywords: layered $SnS_2$ crystals; absorption, reflection and transmission spectra; electronic band structure; optical functions;

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## 1. Introduction

A lot of studies have been devoted to the investigation of the properties of tin dichalcogenides (semiconductors of IV-VI group) and the possibilities of their application for the development of electronic and optoelectronic devices [1 - 7]. Two-dimensional (2D) multi-layered dichalcogenide nanomaterials cause interest because of their attractive properties and possible application in optics, optoelectronics and solar energy conversation [8 - 11]. They have layered structure of X-M-X (S-Sn-S) type with weak molecular Van der Waals bonds between layers and strong chemical bonds inside layers. Unlike graphene with a zero band gap, 2D layered chalcogenide structures have a band gap in the energy range $E > 1$ eV and dichalcogenides in the range $E > 2$ eV. They demonstrate a strong interaction with light waves, which are promising for electronic and optoelectronic instrumentation and solar energy conversion [9 - 14].

According literature data the tin (Sn) and sulfur (S) atoms can crystalize in different forms: the cubic phase of SnS (the spatial groups ***Fm-3m*** and ***F-43m***) [14 - 16], the ***α*** - SnS orthorhombic phase (the spatial group of ***Pbnm***) and ***β*** - SnS phase (the space group ***Cmcm***) [16, 17], the hexagonal phases of $SnS_2$ (the spatial group ***P3m1*** and ***P63/mmc***) [14, 18 - 21] and the $Sn_2S_3$ orthorhombic phase (the space group ***Pnma***) [14]. A low-temperature ***α*** - phase (T < 870°C) and high-temperature



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***β*** - phase (T > 870°C) are formed in orthorhombic crystal lattice. The available experimental data on tin sulphide ($SnS_2$) parameters are very contradictory: the band gaps range from 1.82 to 2.41 eV, and the absorption coefficient is of the order of $10^4$ - $10^5$ $cm^{-1}$ [18 - 21]. Information about the type and nature of electronic transitions responsible for the minimum of the interband gap is also contradictory [17 - 22].

## 2. Experimental methods

$SnS_2$ crystals grown by gas transport method in ampoules were plates that were easily cleave, which made it possible to obtain mirror surfaces of ~ 5x7 mm and different thicknesses from 78 μm to 3 mm. Surfaces of most plates were parallel to the ***b*** axis and recognized visually. Low temperature spectra of crystals deposing in closed helium LTS-22 C 330 optical cryogenic system were measured on spectrometer MDR - 2 with luminosity of 1: 2 and linear dispersion of 7 Å/mm. Photoluminescence measurements were carried out on the double Raman spectrometer DFS - 32 with luminosity of 1:5 and linear dispersion 5 Å/mm and on the double spectrometer SDL - 1 with luminosity of 1:2 and linear dispersion 7 Å/mm. During measurements spectrometers slits do not exceed 30 μm i.e. with resolution around 0.5 meV. All optical system on the base of spectrometers (MDR - 2, DFS - 32 and SDL - 1) are completely automatized and computerized. The typical scheme of measurement equipment on the base of spectrometer SDL - 1 is shown in Fig. 1.

Interference spectra were registered both as usual interference spectra and as wavelength modulated spectra. In the wavelength-modulated spectra, the setup was tuned in such a way that in the middle part of the intensity of the interference signal zero was set and the lower part had a negative value. The electronic system inverts the negative signal in positive one. Example of such spectra is shown in insert of Fig. 1, where ***a*** is minimums of interference fringes of a usual interference spectra and ***b*** is minimums of modified interference spectra. Such system allows us with good accuracy to determine maxima positions. This allow more precise to calculate refractive index. The refractive index calculation method is described in Ref. [23]

## 3. Result and discussions

$SnS_2$ crystals cleaved along the plane of adhesion with mirror surfaces were used for optical transmission (absorption) spectra measurements. Figure 2 shows absorption spectra for crystals of 0.5 mm thickness measured in unpolarized light at temperatures 30 – 300 K and absorption spectra measured at 10 K in E||b and E⊥b polarizations. One can see from received data absorption edge spectra are polarized at temperature 10 K. Edge absorption in E||b polarization begins at lower energies than one in E⊥b polarization. A difference of magnitudes of absorption coefficients for both polarizations in region of high absorption is observed, i.e. the absorption coefficient in E⊥b polarization is less than in E||b polarization. A temperature shift coefficient of edge absorption was estimated ($\boldsymbol{\beta} = \boldsymbol{\Delta E/\Delta T} = 8.275\times10^{-4}$ eV/K).

Figure 3, A shows absorption and wavelength modulated transmission spectra measured for the same crystal of 830 μm in E||b and E⊥b polarizations. A feature E1



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is observed clearly in absorption spectra of both polarizations. Minimal band gap determined from absorption and wavelength modulated transmission spectra is practically identical and reach magnitude of 2.403 eV in both polarizations. This value coincides with results of Ref. [21] (2.41 eV) and close to data from Ref. [3] (2.308 eV – indirect and 2.554 eV – direct). The character of electron transitions responsible for minimum bang gap Eg is determined as indirect by all analyzed references, but a magnitude of band gap is differ: 2.23 [1], 2.25 eV [2], 1.82 eV [18], 2.07 eV [19], 2.2 eV [20], 2.24 eV [22]. This is due to the fact that thick crystals are required to determine the magnitude of indirect transitions, while most of the experimental measurements are performed on thin films.

It is well known that the thick crystals are necessary for indirect transitions investigations (usually with thickness around 1mm). In our case the sample of 830 μm thickness was used for absorption investigation in the region of indirect transitions. The thinner samples (thickness 78 μm) were used for absorption studying in the region of direct transitions. Figure 3A shows spectra in the region of indirect transitions and figure 3B shows spectra in the region of direct transition.

A weak feature is observed at 2.6 eV in E⊥b polarization both as intractable shoulder in absorption spectra and as E2 maximum in $\Delta T/\Delta\lambda$ spectra. Figure 3, B shows absorption (K) and wavelength modulated transmission ($\Delta T/\Delta\lambda$) spectra of crystals with 78 μm thickness measured in the same polarizations. As can be seen from the figure in crystals of small thickness, the absorption spectra are polarized and in E⊥b polarization the absorption curve has a gentler spectrum than in E||b polarization. These results indicate that minimal direct energy gap ($E_g^d$ – 2.6 eV) is due to direct allowed transitions in E||b polarization and to forbidden transitions in E⊥b polarization. These features appear in wavelength modulated spectra as maxima $E2^b$ (2.623 eV) and $E2^a$ (2.698 eV).

A well pronounced interference at energy interval 1 - 2.4 eV are observed in transmission and reflection spectra measured at temperatures 10 K and 300 K. Spectral dependences of refractive indices ($n$) were calculated from interference transmission spectra (see Fig. 4A). Calculations were carried out by two methods as described previously in chapter "Experimental methods". Calculated values are almost completely coincided. The insert of fig. 4A shows the determination maximums positions (a1) and zero values position (a2) of interference transmission spectra. The received data are used for refraction index calculation according equations from Ref. [23]. A weak rise of refractive index is observed at energy increasing. Reflection spectra of 78 μm thickness crystal were measured at 10 K in energy interval 2.2 - 2.9 eV (see Fig. 4, B). No featured observed in reflection spectra nearby E1 maximum. A weak maximum with amplitude 4 – 5 % is observed in reflection spectra in E||b polarization at energies of E2. In E⊥b polarization this maximum is not recognized. Since mainly direct electron transitions are observed in the reflection spectra, we assume that the feature E2 in the polarization E||b is due to direct allowed transitions with small oscillator strength. This is also confirmed by the character of the absorption curves shown in Fig. 3.

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Maxima in the region of edge absorption beginning (transitions E1) are not observed in the reflection spectra measured at temperatures 300 K and 10 K in non-polarized and polarized light. This indicates that the edge absorption and the E1 feature are formed by indirect transitions. And E2 transitions in E⊥b polarization are due to the direct forbidden transitions. Reflectivity maxima a1 are observed in spectra measured at temperature 10 K on positions 3.301 eV and 3.318 eV for E⊥b and E||b polarizations, respectively (see Fig. 5, B). At room temperature these maxima are observed with weaker intensity at energies 3.190 eV (non-polarized) and 3.198 eV (E||b polarization).

The amplitude of reflection coefficient $\boldsymbol{R}$ is related with phase $\boldsymbol{\varphi}$ by the next relation [24, 25]:

$$r = \sqrt{R}e^{-i\varphi} \qquad (1)$$

The spectral dependence of reflection coefficient R and optical constants $\boldsymbol{n}$, $\boldsymbol{k}$, $\boldsymbol{\varepsilon_1}$ and $\boldsymbol{\varepsilon_2}$ have the next ratio:

$$\begin{cases} r = \frac{N-1}{N+1} = \frac{n+ik-1}{n+ik+1} \\ r = \sqrt{R}e^{-i\varphi} = \sqrt{R}(\cos\varphi - i\sin\varphi) \end{cases} \begin{cases} n = \frac{1-R}{1-2\sqrt{R}\cos\varphi+R} \\ k = \frac{2\sqrt{R}\sin\varphi}{1-2\sqrt{R}\cos\varphi+R} \end{cases} \begin{cases} \varepsilon_1 = n^2 + k^2 \\ \varepsilon_2 = 2nk \end{cases} \qquad (2)$$

The amplitude value of reflection coefficient should be determined simultaneously with its phase for each wavelength i.e. $R \approx R(\omega)$ and $\varphi = \varphi(\omega)$. The phase of reflected beam is related with the reflectivity amplitude by Kramers-Kronig integral:

$$\varphi(\omega_0) = \frac{\omega_0}{\pi}\int_0^\infty \frac{\ln R(\omega)}{\omega_0^2 - \omega^2} d\omega \qquad (3)$$

For determination of reflected beam phase from experimentally measured reflectivity it is necessary to write a spectrum in infinity diapason of frequencies. But recorded spectra are determined by the set-up confines and one can measure spectra in certain spectral range. Usually the amplitude of measured reflection spectra changes drastically near the feature $\boldsymbol{\omega_0}$ and in over parts of the spectrum it monotonous increases or decreases. Thereby one can take integral (3) in parts. First the integral is calculated for region of measured reflection coefficient (from $\boldsymbol{\omega_a}$ to $\boldsymbol{\omega_b}$). In high energy region $\boldsymbol{\omega_b} \le \boldsymbol{\omega} \le \boldsymbol{\infty}$ (where reflectivity is not measured) the extrapolation of reflection spectra was made by function $R = c\omega^{-p}$ where $\boldsymbol{c}$ and $\boldsymbol{p}$ are constant. Substituting this function into the integral (3) and solving it the phase value for the given region is found. In the region $0 \le \boldsymbol{\omega} \le \boldsymbol{\omega_a}$ an approximation $R(\omega) = R(\omega_a)$ is used for the phase calculation. In this case the influence of lattice vibrations on reflection spectra is neglected because it do not give significant contribution in $\boldsymbol{R}$ spectra.

The experimentally measured values of $\boldsymbol{R}$ and calculated $\boldsymbol{\varphi}$ are allowed to determine optical functions ($\boldsymbol{n}$, $\boldsymbol{k}$, $\boldsymbol{\varepsilon_1}$ and $\boldsymbol{\varepsilon_2}$) in energy interval from 2 to 3 eV. This is done to compare the refractive index $\boldsymbol{n}$ spectral dependences obtained from interference and reflection spectra. The refractive index magnitude at energy of 2.2 eV is equal to 3.4 according results of both calculations. As was to be expected at 2.5 - 2.6 eV, i.e. in the region of E2 transitions, changes in the optical functions $\boldsymbol{n}$, $\boldsymbol{k}$, $\boldsymbol{\varepsilon_1}$ and $\boldsymbol{\varepsilon_2}$ spectral characteristics are observed. This confirms the direct transitions



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nature responsible for E2 maximum.

In the depth of the absorption band in the region 3 - 6.5 eV at 300 K, four maxima a1 - a4 were observed in the reflection spectra of $SnS_2$ crystals in unpolarized light (see Fig. 7, A). These maximums are due to electron transitions between conduction and valence bands.

Maxima energy positions show in Figure 7. Maxima a1 and a2 have weaker intensites in comparison with maxima a3 and a4. One can see also in abovementioned figure and the spectral dependences of optical constants in the same enerty region. Figure 8 shows esitmated localization of these transitions in the framework of teoretically calcualted band structie [2] of $SnS_2$ crystals. The direct transitions take place in the center of Brillouin zone since in Γ point the maxima of vlence bands and the minima of conduction bands are localized. The energy interval caused by the indirect transitions Γ – M is practically unobserved due to the proximity of the direct transitions $E2^a$ and $E2^b$ values in the Brillouin zone center.

## 4. Conclusions

It was established by the investigation of absorption, reflection and wavelength modulated transmission spectra of hexagonal phase $SnS_2$ crystals (space group $P6_3/mmc$) in temperature interval 10 – 300 K that the minimal bang gap is due to indirect transitions between points Γ and L ($E_g^{ind}$ = 2.403 eV). The transitions appear at the same energies in both polarizations (E||b and E⊥b). The minimal direct energy interval ($E_g^{dir.allow.}$ = 2.623 eV) in E||b polarization is formed by direct allowed transitions and in E⊥b polarization ($E_g^{dir.forb.}$= 2.698 eV) it is formed by direct forbidden transitions in Γ point of Brillouin zone. The refractive index $n$ changes in interval 3 – 4 and has a maximum at 2.6 eV. The optical functions ($n$, $k$, $\varepsilon_1$ and $\varepsilon_2$) for energies $E > E_g$ (3 – 6.5eV) were calculated from reflection spectra by Kramers-Kronig analysis. The localization of observed electron transitions in the theoretically calculated band structure is suggested.

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## Figures captions

Fig. 1 Experimental setup on the base of spectrometer SDL - 1. Insert shows the modified interference spectrum.

Fig. 2 Absorption spectra of hexagonal phase $SnS_2$ crystals with thickness 0.5 mm measured at different temperatures (300 - 30 K) in unpolarized light and at temperature 10 K in E||b and E⊥b polarizations.

Fig. 3 Absorption (***K***) and wavelength modulated transmission ($\Delta T/\Delta\lambda$) spectra of $SnS_2$ crystals of hexagonal phase measured at temperature 10 K in E||b and E⊥b polarizations on samples with thicknesses 830 μm (A) and 78 μm (B). Curves for E⊥b polarization are shifted down on 200 $cm^{-1}$ for clarity.

Fig. 4 A - Refractive indices n(a1) and n(a2) spectral dependences calculated from interference fringes of transmission by maxima (a1) and by minima (a2). B - Reflection spectra of $SnS_2$ crystals measured at temperature 10 K in non-polarized light (n/p) and in E||b and E⊥b polarizations in the region of edge absorption beginning. Inserts show determination of extremes for refractive indices calculation.

Fig. 5 Reflection spectra of $SnS_2$ crystals measured at room temperature (A) and 10 K (B) in non-polarized light and E||b and E⊥b polarizations.

Fig. 6 A – Spectral dependences of absorption coefficient (***K***), refractive index (***n***) and extinction coefficient (***k***) for E||b polarization and temperature 10 K. B – Real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of permittivity.

Fig. 7 Reflection (***R***) spectra measured at room temperature and calculated spectra of absorption (***K***), refractive index (***n***), extinction coefficient (***k***), real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of permittivity.

Fig. 8 The structure of the energy bands of hexagonal $SnS_2$ crystals (polytype 2H, space group $P6_3/mmc$). The inserts showthe Brillouin zone and the atomic layers position and the crystalline axes directions [2].

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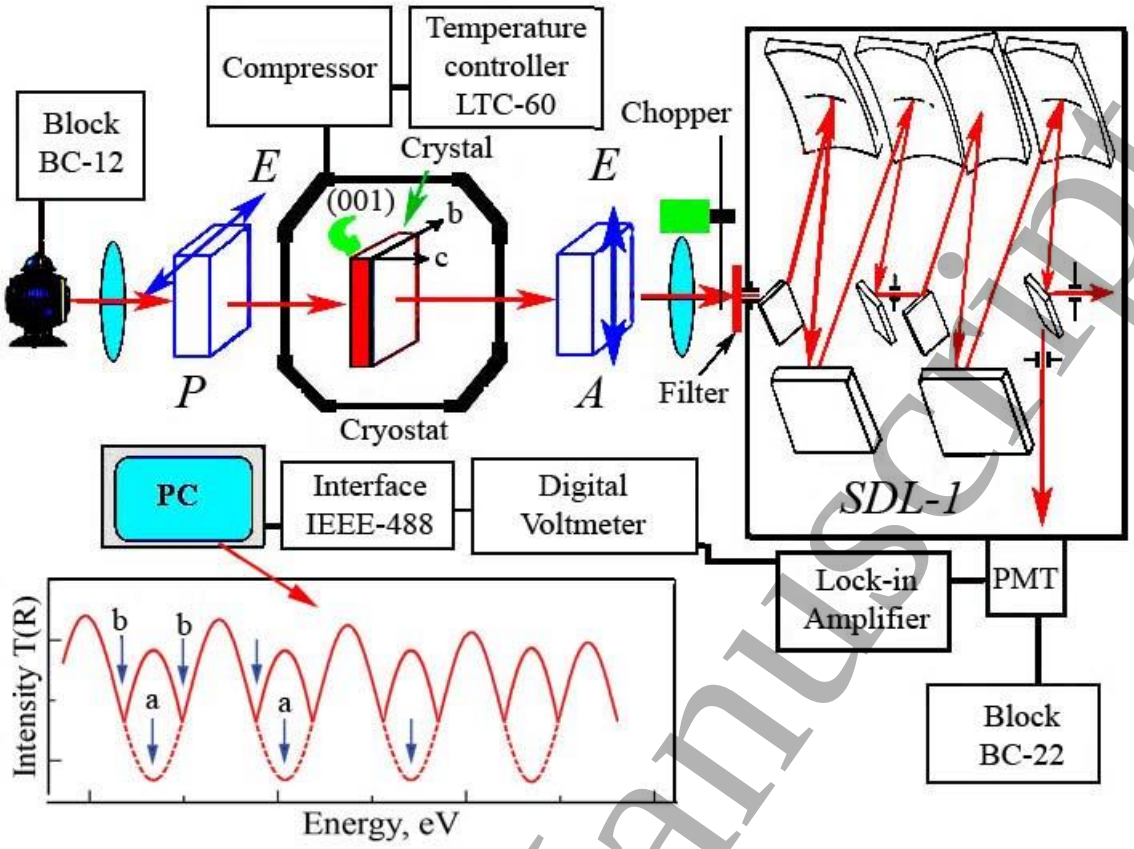


Fig. 1

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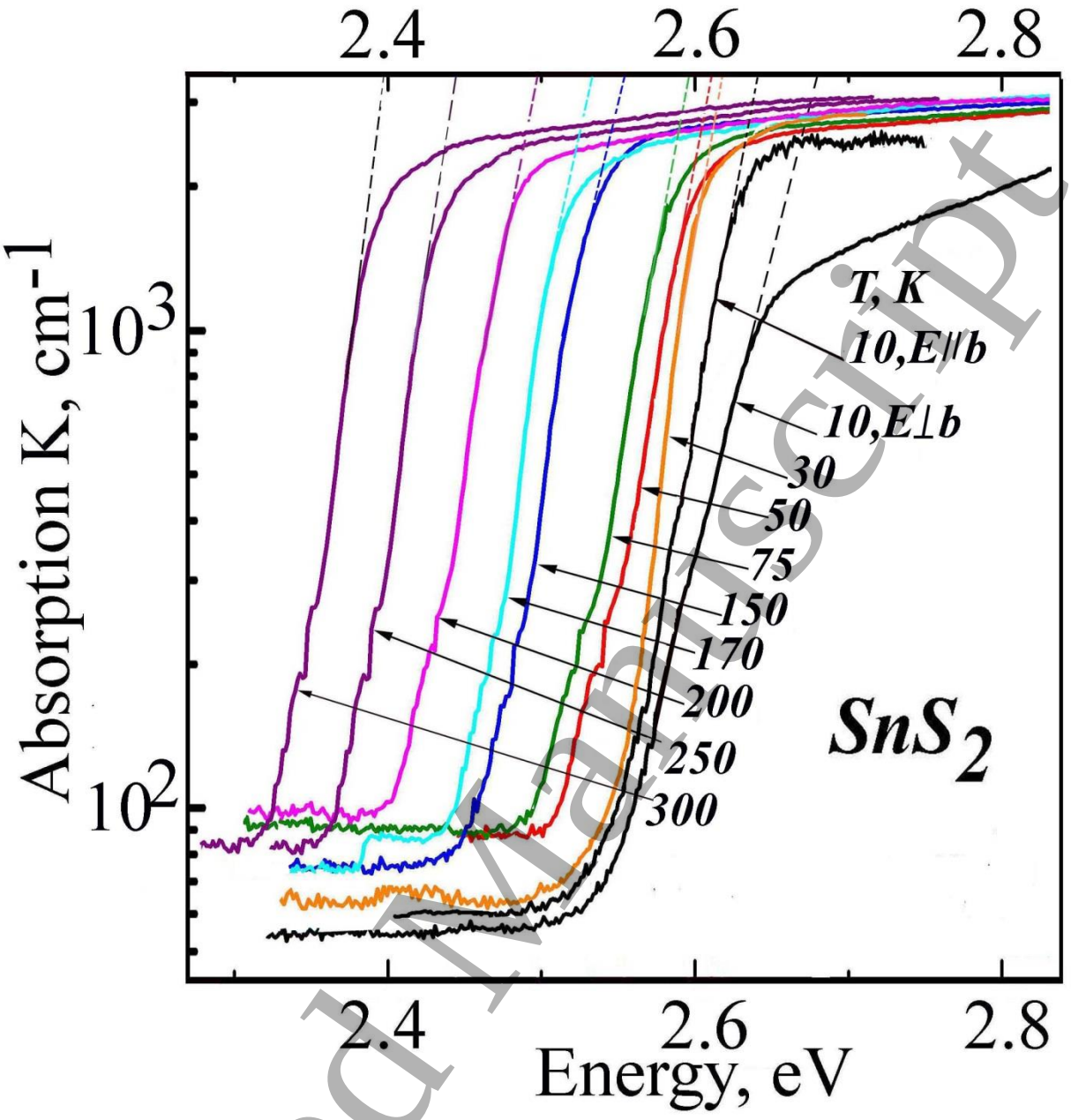


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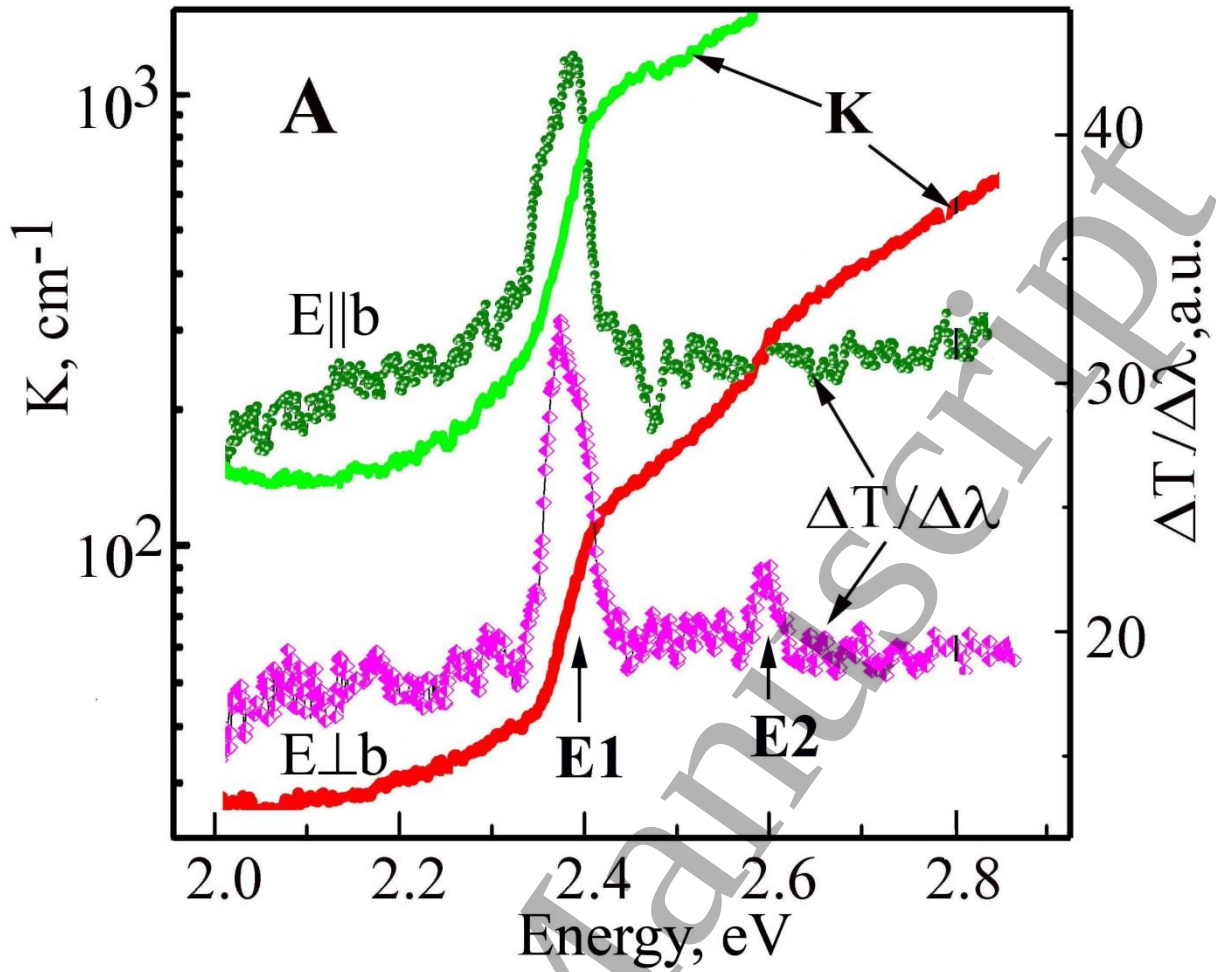


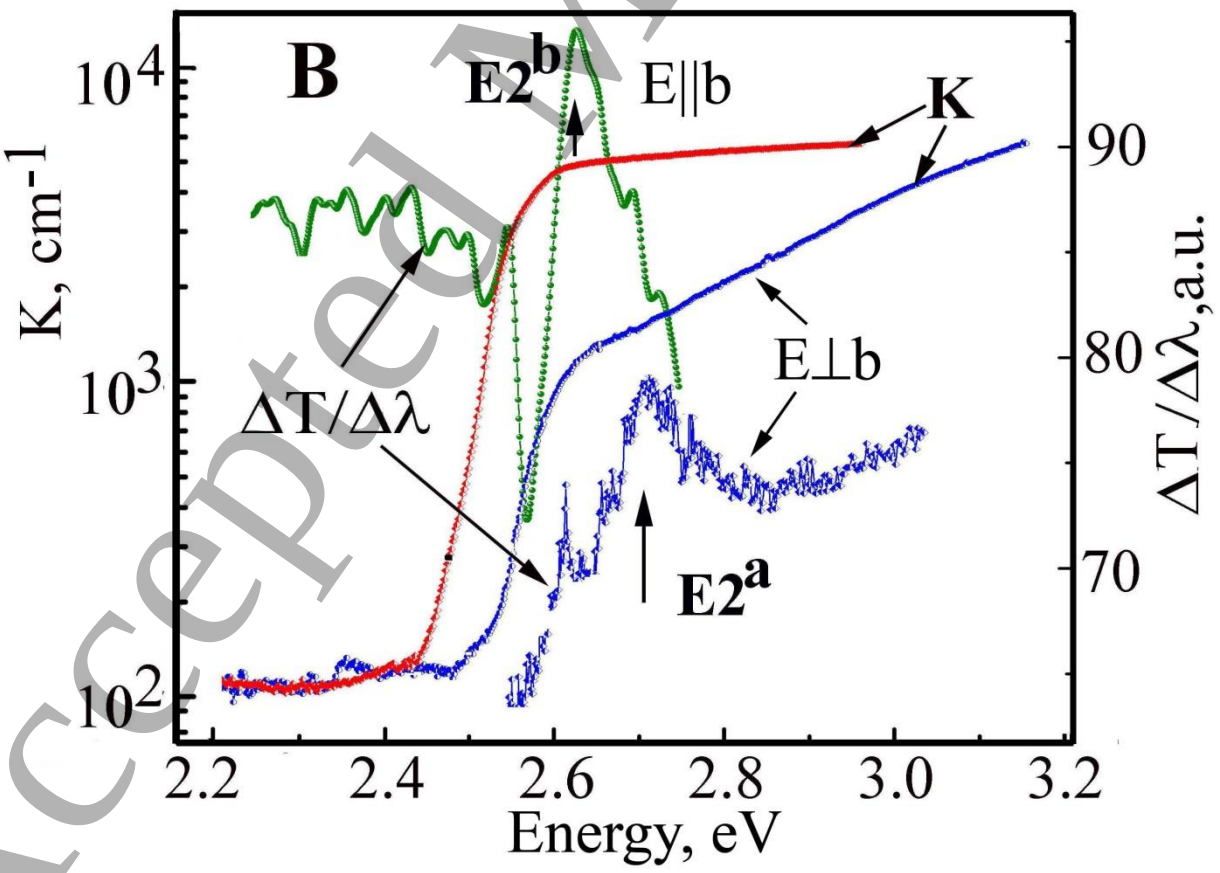


Fig. 3



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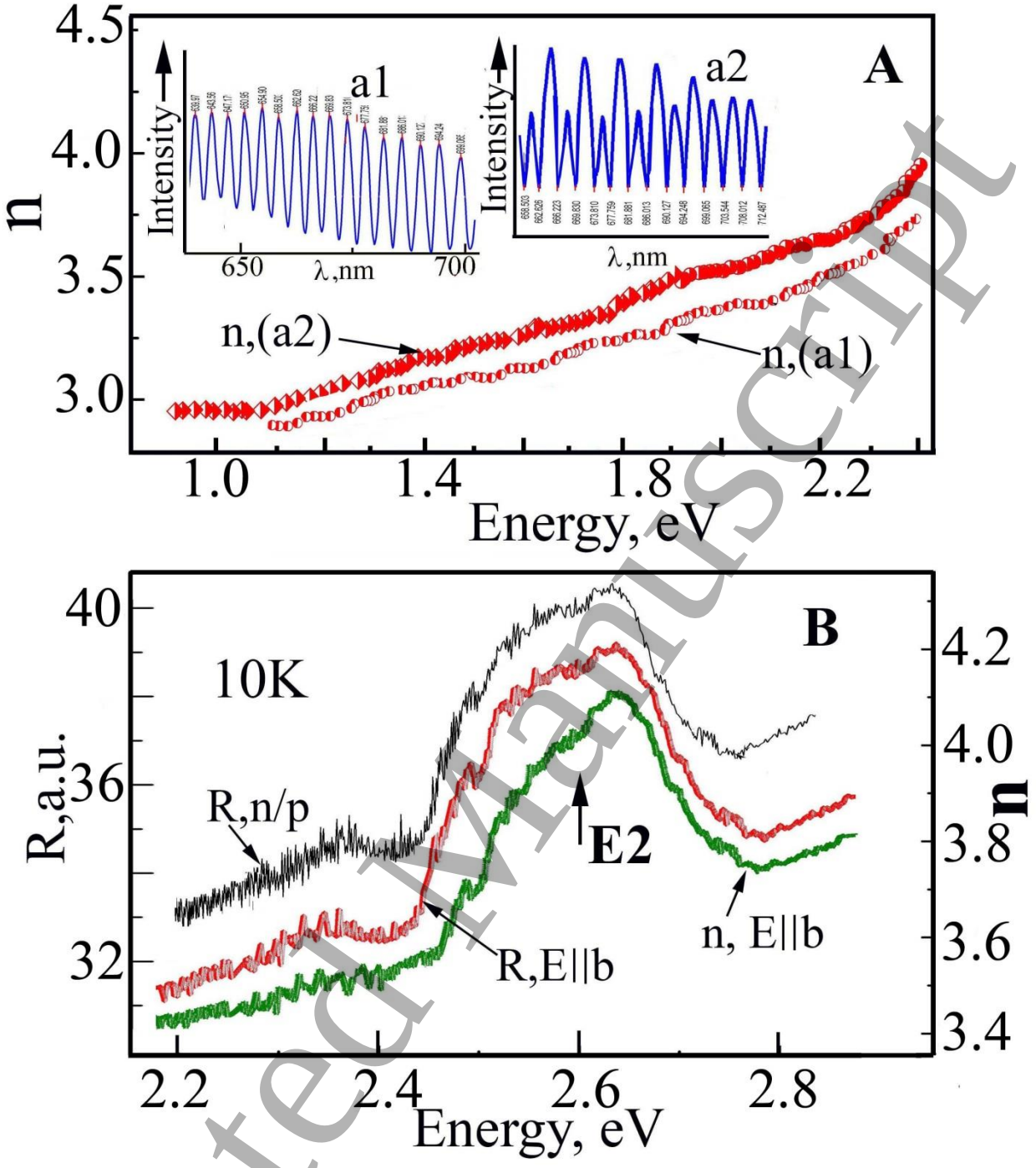


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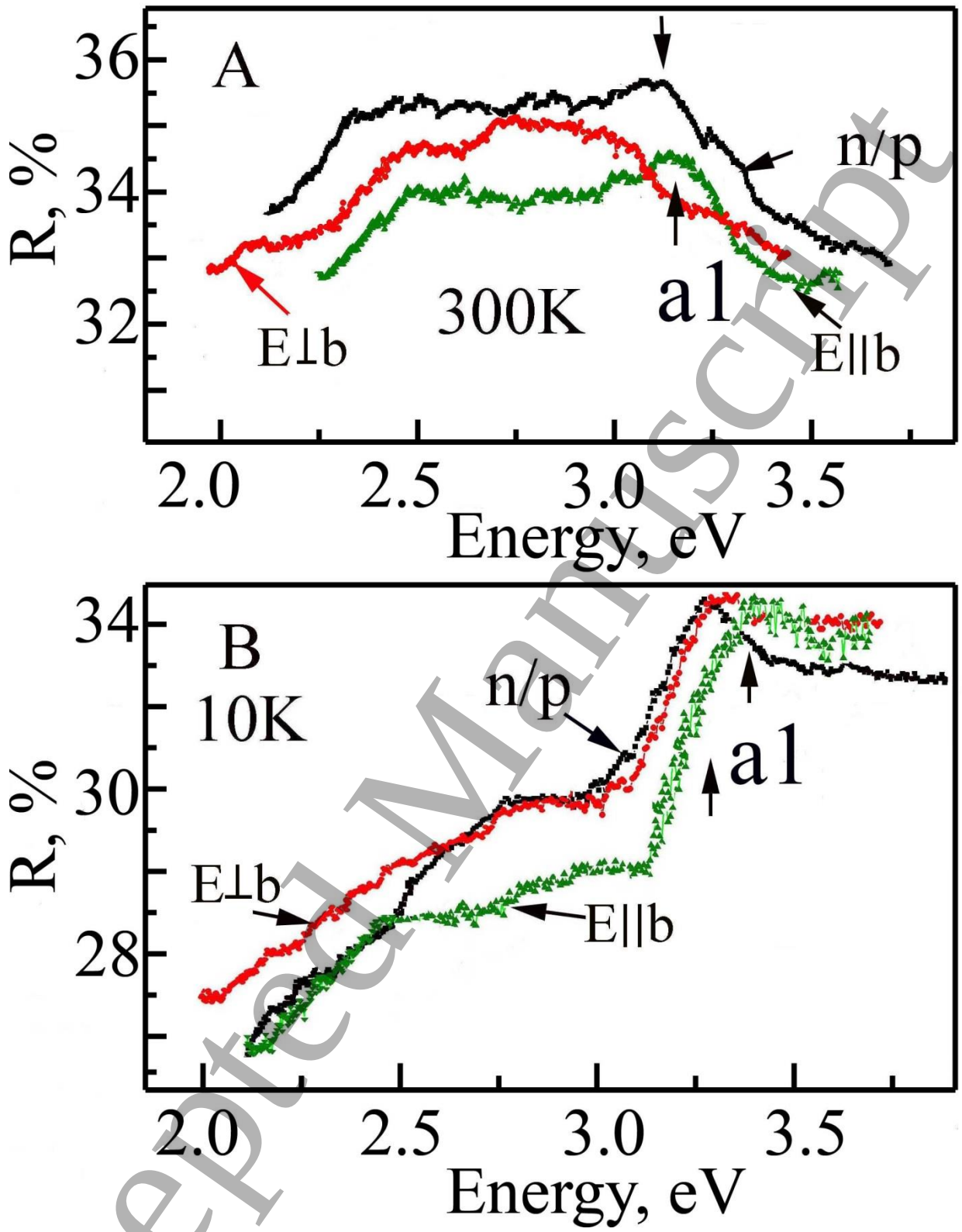


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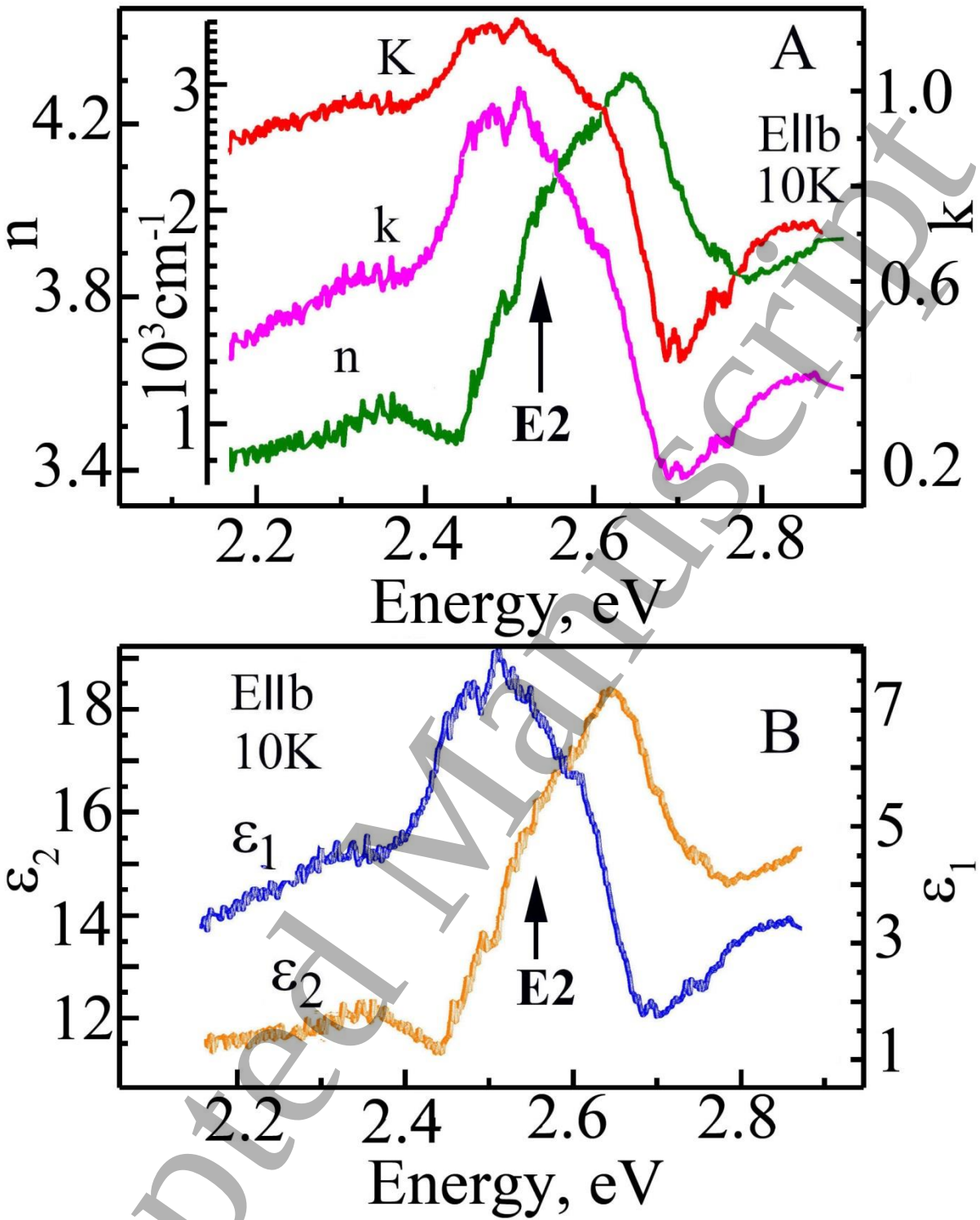


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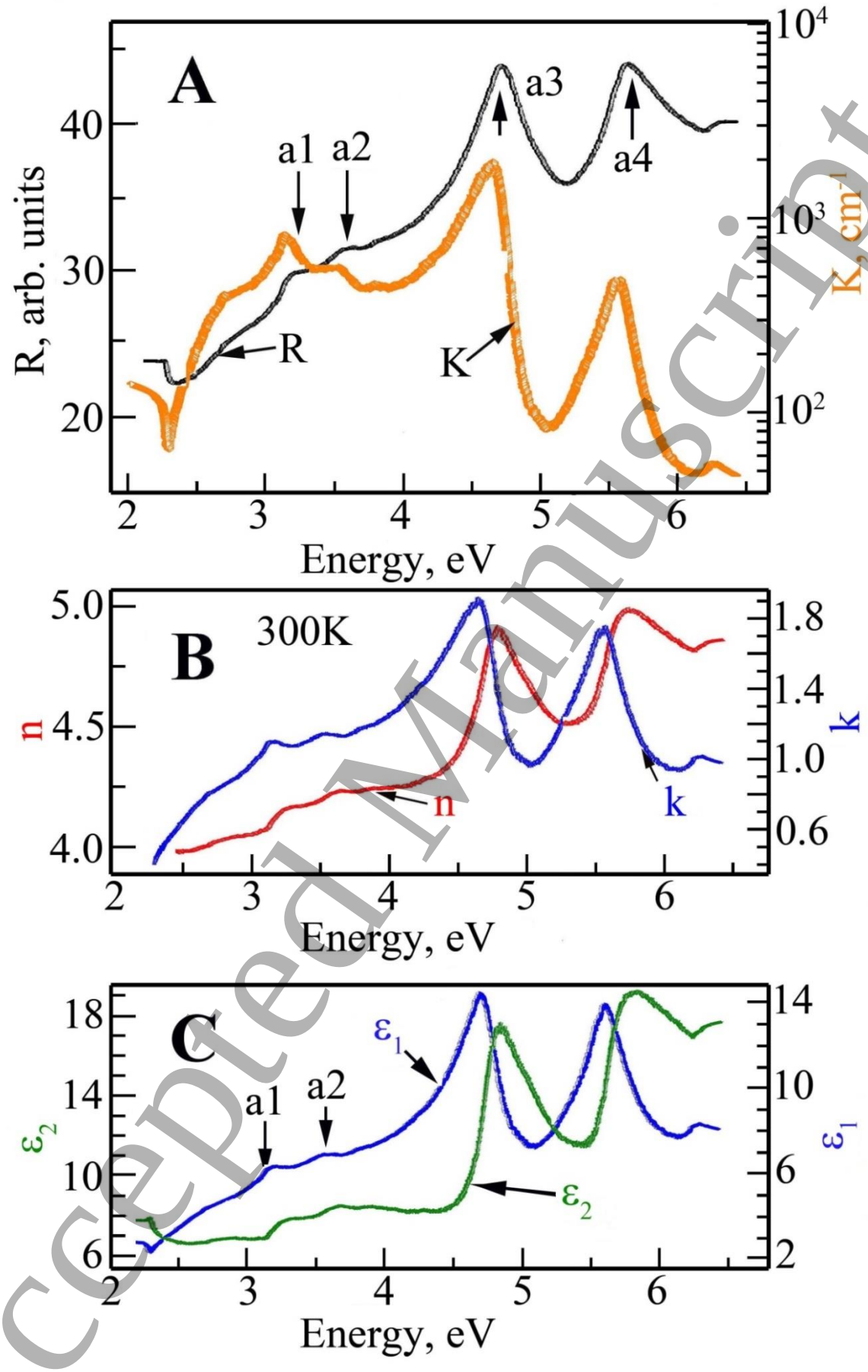


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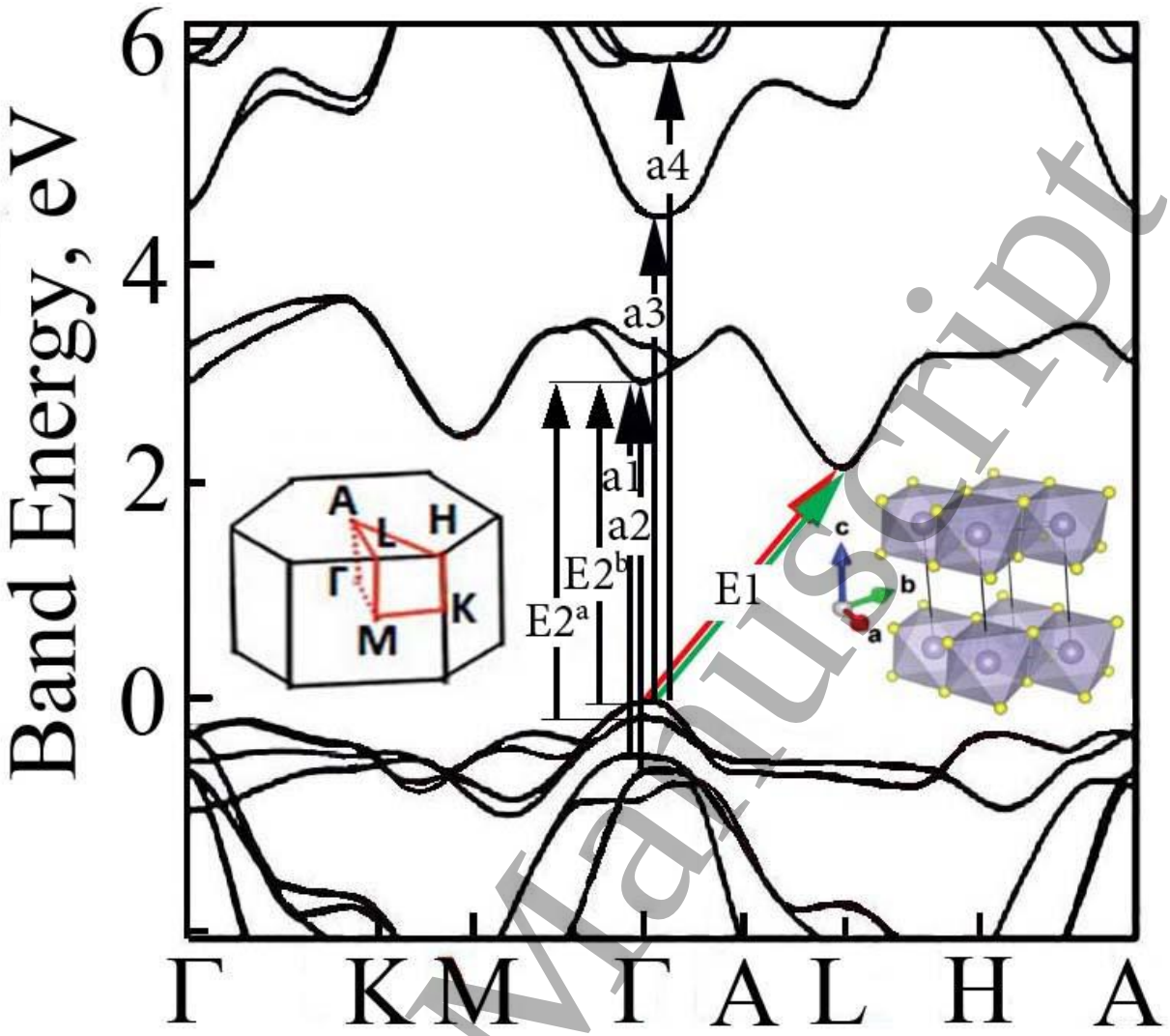


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