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# Temperature dependence of FT-IR absorption and Raman scattering of copper phthalocyanine thin layers deposited on silicon substrate

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## Abstract

The temperature study of FT-IR absorption and Raman scattering spectra of vacuum deposited CuPc thin layers are presented. Thin films have been prepared by thermal deposition of CuPc layer onto (001) Si substrate. The FT-IR absorption and Raman scattering studies have been performed in the temperature range 77–523 K and 298–513 K, respectively. The Raman spectra were obtained at room temperature in quasi back-scattering geometry. The orientation of molecules in the layers were determined by the method described in our previous paper using polarization analysis of the Raman spectra [14]. The obtained results from Raman experiment are compared with FT-IR absorption spectra of CuPc molecules in KBr pellets and thin layers of CuPc on (001) Si substrate. The change of the intensity, band position and full width at half maximum (FWHM) of Raman and FT-IR modes versus temperature during heating and cooling procedure have been investigated. It has been revealed the fast decrease of the frequency and the intensity of these modes during increase the temperature above 300 K. Some anomalies in temperature dependencies of integrated intensity and FWHM for modes observed in FT-IR absorption and Raman scattering spectra have been observed at 270 K (in FT-IR) and 480 K (in Raman and FT-IR) indicating the change of the structural form. © 2005 Elsevier B.V. All rights reserved.

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Keywords: Copper phthalocyanine (CuPc); Thin films; FT-IR spectra; Raman spectra

## 1. Introduction

Copper phthalocyanine (CuPc) as the transparent and hole transporting layer is used in wide variety of technological applications including electroluminescence devices, sensor devices, optical waveguides and many others [1]. Moreover, CuPc layers have caused a great deal of interest due to their low cost and potentially high photoelectrical properties [1,2]. Because the electrical as well as the optical properties of the CuPc layers are highly depending on the structural orientation of CuPc molecules, the knowledge of crystalline structure and point defects

appearing during deposition process are very important for successful application in electrical and optical devices. Some properties, such as high photoconductivity, considerable changes in the conductivity under gas adsorption, thermal dependent conductivity in charge-coupled devices were not explained so far [3].

Orientation of the molecular CuPc thin film deposited on different substrates have been estimated using a different experimental methods [4–12]. The copper phthalocyanine exists in several molecular forms, but the most known are the  $\alpha$ - and  $\beta$ -forms. For the vacuum deposition processes, the  $\beta$ -form is more thermodynamically stable than the  $\alpha$ -form. CuPc films deposited onto substrates are usually of the  $\alpha$ -phase but undergo the phase transformation to the  $\beta$ -phase during annealing procedure at higher temperatures.

In this paper, we present experimental results of temperature study of FT-IR absorption and Raman scattering spectra of vacuum deposited CuPc films on (001) Si

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substrate. The change of the intensity, band position and full width at half maximum (FWHM) of Raman and FT-IR modes versus temperature during heating and cooling procedure have been investigated.

## 2. Theory

Recently, many attention has been paid to the CuPc inorganic heterostructures due to their applications in optoelectronics and microelectronics devices. These structures are also interesting research subject for photovoltaic applications. Because of these reasons the optical and transport properties of the interfacial properties, became important [11,12]. CuPc is reported to have nine polymorphous forms but  $\alpha$ - and  $\beta$ -ones are most important forms for the crystallization using a vacuum deposition method [4]. The influence of the kind of the substrate and their temperature on the growth morphology of CuPc layers is still not well recognized and understood. For example, the unit cell parameters for  $\alpha$  and  $\beta$  forms are as follows: for  $\alpha$ -form of bulk crystal with triclinic system:  $a = 1.2886$  nm;  $b = 0.3769$  nm;  $c = 1.2061$  nm;  $\alpha = 96.2^\circ$ ;  $\beta = 90.6^\circ$ ;  $\gamma = 90.3^\circ$ . For  $\alpha$ -form of CuPc epitaxial film on (001) KCl with triclinic system:  $a = 1.291$  nm;  $b = 0.381$  nm;  $c = 1.200$  nm;  $\alpha = 95.6^\circ$ ;  $\beta = 90.1^\circ$ ;  $\gamma = 91.0^\circ$  [6], and for  $\beta$ -form; space group  $P2_1/a$ ;  $a = 1.941$  nm;  $b = 0.479$  nm;  $c = 1.463$  nm;  $\beta = 120.56^\circ$  [7].

In particular, the chemical nature, lattice constant (or amorphous structure) and surface geometry of the substrate are important parameters [8–10].

It has been revealed that the orientation, also the temperature dependencies of thin CuPc layers can be determined using the analysis of external and internal molecular vibrational modes connected with symmetry of CuPc molecule [8–10,13,14].

The orientation of CuPc molecules in thin layers has been determined by measuring the bands intensity of C–C and C–N bond stretching vibrations in different scattering geometry (VV, VH) (see Fig. 1) [8,9,15,16].

It has been reported by Basova and Kolesov [17] that the weakness of the intermolecular interactions in CuPc crystal causes that spectra of internal vibrations of crystalline CuPc are very similar to the spectra of the free molecule.

The vibrations of the CuPc planar molecule (see Fig. 1) which consists of 57 atoms and possessing  $D_{4h}$  point group symmetry can be classified into following irreducible representation (taking into account only internal vibrations) [10,17,18]:

$$\Gamma_{\text{vib}} = 14A_{1g} + 13A_{2g} + 14B_{1g} + 14B_{2g} + 13E_g \\ + 6A_{1u} + 8A_{2u} + 7B_{1u} + 7B_{2u} + 28E_u \quad (1)$$

where  $A_{1g}$ ,  $B_{1g}$ ,  $B_{2g}$ , and  $E_g$  modes are Raman-active. The nondegenerate  $A_{1g}$ ,  $B_{1g}$ , and  $B_{2g}$  modes are in-plane vibrations, and double degenerate  $E_g$  are the out-of-plane

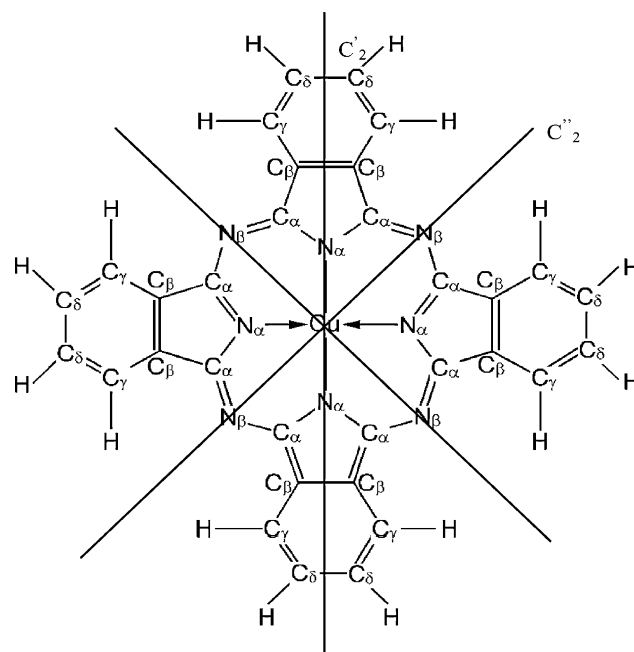


Fig. 1. The molecular structure and atomic notation of CuPc molecule.

vibrations. In the case of  $B_{1g}$  vibrational modes, the atomic shifts are symmetric relative to the twofold axes  $C_2'$  passing through the central copper atom, and the benzene rings. In the case of  $B_{2g}$  vibrational modes, the atoms are shifted symmetrically relative to the  $C_2''$  axes passing through the  $N_b$  atoms (Fig. 1) [17].

## 3. Experimental

The preparation of the copper phthalocyanine (CuPc) layers has been described in detail previously [14]. The CuPc layers used in our experiments have been deposited onto n-type (001) Si substrates in vacuum chamber of pressure  $2 \times 10^{-4}$  Pa. The deposition rate was 0.2 nm/s.

To check the existence of the phase transition in the thin CuPc layers, the temperature dependencies of Raman scattering and FT-IR absorption studies have been performed.

The FT-IR absorption spectra of CuPc samples pelletized with KBr were studied using the Perkin-Elmer Spectrum 2000 spectrophotometer. The spectra were recorded in the region from 4000 to 600  $\text{cm}^{-1}$  with a resolution of 1  $\text{cm}^{-1}$ . The FT-IR absorption spectra have been performed in the temperature range 77–523 K with an accuracy  $\pm 1$  K without breaking pressure. The measured samples were placed in vacuum cryostat with pressure 0.1 Pa. To ensure correct measurements the temperature was stabilized at least ten minutes before each measurement. The Raman spectra were obtained in different temperature using quasi back-scattering geometry [14] in the temperature range 298–513 K during heating and cooling process. The spectra

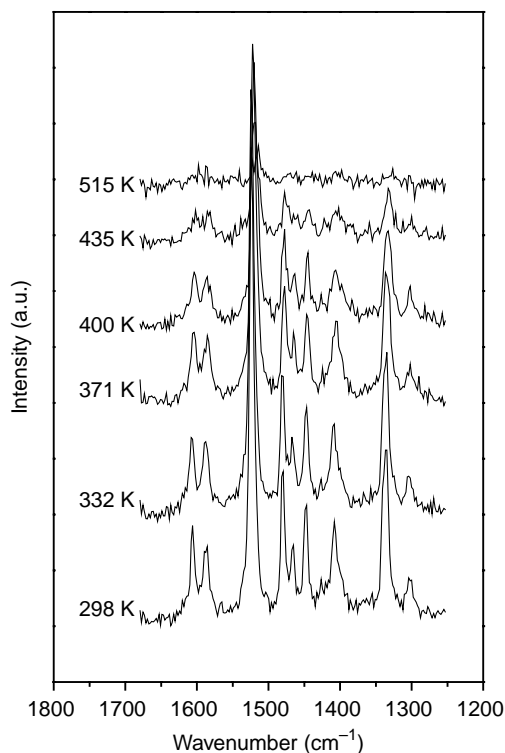


Fig. 2. The Raman spectra of CuPc thin film grown on (001) Si substrate obtained at different temperatures.

were recorded in the region from 1250 to 1700  $\text{cm}^{-1}$  with resolution of 2  $\text{cm}^{-1}$ .

The intensities of Raman bands were reduced using Bőse–Einstein population factor [14]. The analysis of the Raman spectra was performed using a curve-fitting method with Lorentzian components. The background line in spectra produced by quasi-elastic wing and the luminescence of some samples, was subtracted by linear approximation.

#### 4. Results and discussion

The Raman spectra obtained at different temperatures during heating process in the quasi back-scattering geometry of CuPc film grown on (001) Si substrate are presented in Fig. 2. During the cooling process, the Raman spectra show similar changes at different temperatures, but differ in the quantitative manner. Almost all of the Raman modes of CuPc [14] are present in measured Raman spectra. The integral intensity, band position and the FWHM of selected Raman-active modes were determined using the Lorentzian line shape fitting. From the spectra of CuPc obtained at different temperatures, changes of bands position, FWHM and integral intensity of the Raman bands are clearly evident. The symmetry of these modes belongs to  $A_{1g}$  and  $B_{1g}$ , respectively. From the spectra (see Fig. 2) we can see that the modes related to  $A_{1g}$  symmetry are basically stronger than those of  $B_{1g}$ , and the enhancement (or suppress) behavior of the integral intensity

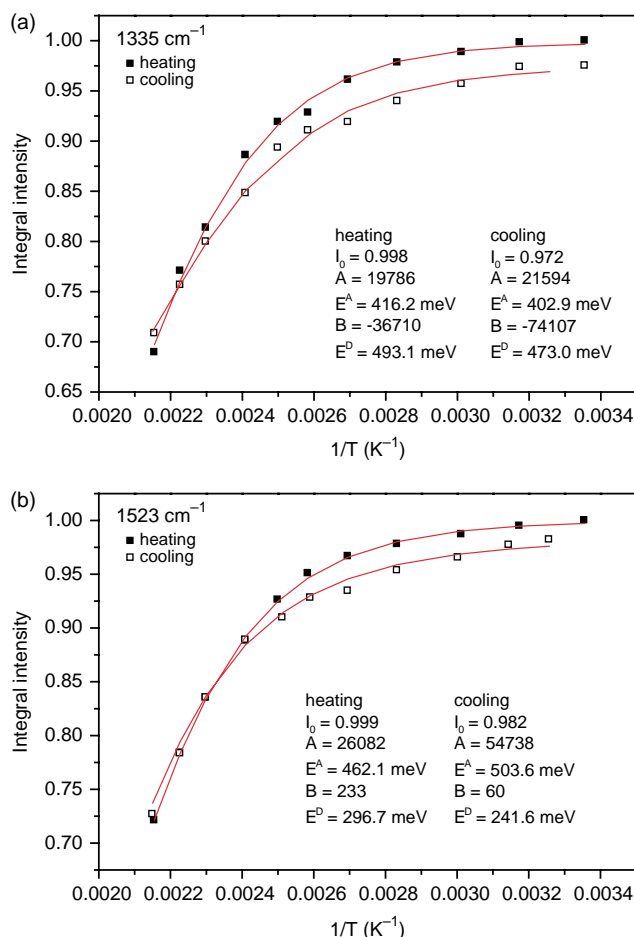


Fig. 3. The integral intensity of the 1335  $\text{cm}^{-1}$  (a) and 1523  $\text{cm}^{-1}$  (b) Raman modes versus reciprocal temperature of CuPc film grown on (001) Si substrate. The solid curves represents the fit to the data using Eq. (2).

with temperature differs greatly between the modes belonging to different symmetries [14].

The dependencies of the integral peak intensity in both, heating and cooling process versus temperature for Raman modes at 1335 and 1523  $\text{cm}^{-1}$  are presented in Fig. 3a and b, respectively.

The temperature dependence of the mode integral intensity can be expressed as:

$$I(T) = \sum_i \frac{I_{0i}}{1 + A_i e^{E_i^A/k_B T} + B_i e^{E_i^D/k_B T}}, \quad (2)$$

where  $I_{0i}$  is the mode intensity at 0 K,  $E_i^A$  and  $E_i^D$  are energies of deactivation transitions,  $A_i$  and  $B_i$  are fitting parameters for different phase transitions. The solid lines in Fig. 3a and b are obtained by fitting procedure using Eq. (2). On these figures the estimated values  $E^A$  and  $E^D$  are presented.

The dependencies of Raman bands position at 1335 and 1523  $\text{cm}^{-1}$  of CuPc layer on Si substrate as a function of temperature while heating from room temperature to 515 K and then cooling to room temperature are presented in Fig. 4a and b, respectively. These temperature dependencies

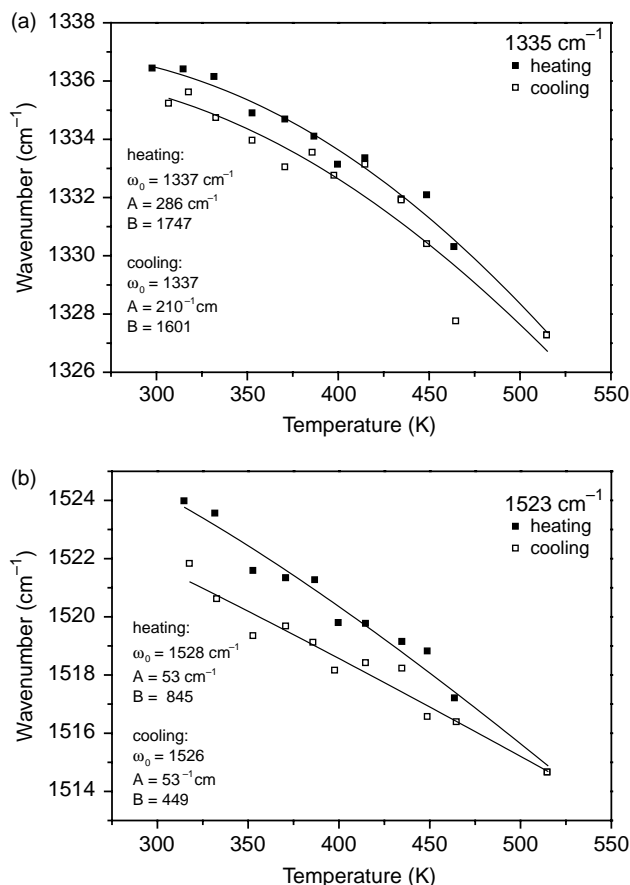


Fig. 4. The temperature dependence of the frequency of the CuPc Raman bands at  $1335\text{ cm}^{-1}$  (a) and  $1523\text{ cm}^{-1}$  (b). The solid curves are the least-squares fittings of the experimental data using Eq. (3).

of the Raman shift  $\omega(T)$  for CuPc layers can be described by expression [17]:

$$\omega(T) = \omega_0 - \frac{A}{e^{\hbar B \omega_0 / k_B T} - 1} \quad (3)$$

where  $\omega(0)$  is the Raman phonon frequency at 0 K,  $k_B$  the Boltzmann constant,  $T$ —temperature,  $\hbar$ —the Planck constant/ $2\pi$  and  $A$  and  $B$  are imposed fitting parameters. The solid curves in Fig. 4a and b represent the fits to the data using Eq. (3). As it can be seen from Fig. 4a and b, the observed data fit this functional form quite reasonable.

Fig. 5a and b show the temperature dependence of the Lorentzian broadening parameter,  $\Gamma$ , i.e. the FWHM, for the  $1335$  and  $1523\text{ cm}^{-1}$  modes of CuPc. It is known, that the band transition thresholds decrease in proportion to the Bose–Einstein factors for the sum of phonon emission and absorption [9,19].

With the increase of the temperature, the exciton transition in semiconductors is broadened by LO phonon scattering, and the temperature-dependent exciton linewidth ( $\Gamma$ ) can be described by the sum of the temperature-independent inhomogeneous term ( $\Gamma_i$ ) and the temperature-dependent homogeneous term ( $\Gamma_h$ ). The latter is the product of exciton-LO phonon coupling strength ( $\Gamma_c$ )

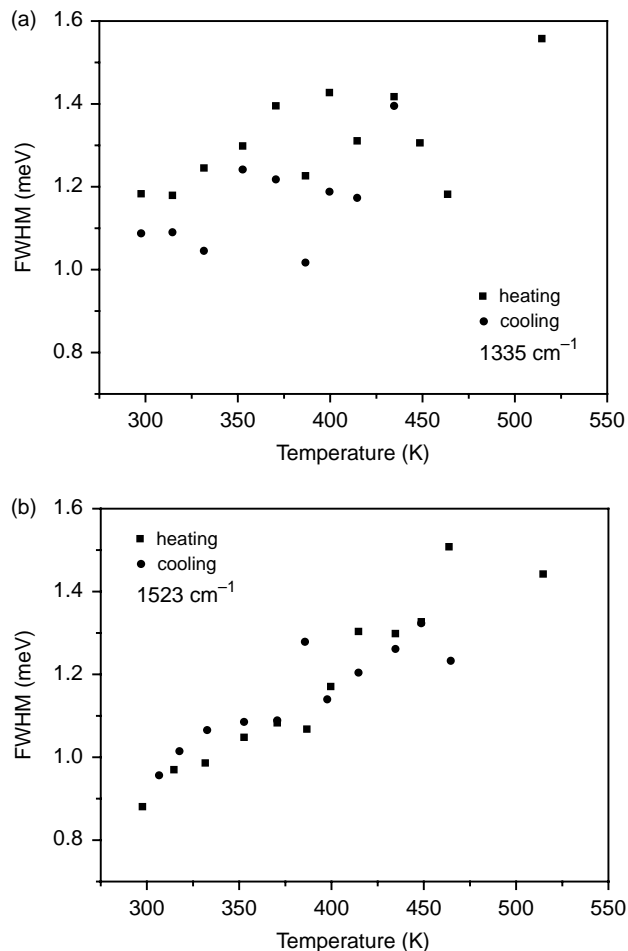


Fig. 5. The dependence of the Lorentzian broadening parameter  $\Gamma$  on the temperature for the  $1335\text{ cm}^{-1}$  (a) and  $1523\text{ cm}^{-1}$  (b) modes of CuPc.

and the LO-phonon population ( $N_{LO}$ ):

$$\Gamma = \Gamma_i + \Gamma_h, \quad (4)$$

where

$$\Gamma_h = \Gamma_c N_{LO} = \Gamma_c (e^{\hbar \omega_0 / k_B T} - 1)^{-1}$$

Thus, the temperature dependence of  $\Gamma$  in CuPc can be expressed as [20]:

$$\Gamma(T) = \Gamma_0 \left[ 1 + \frac{2}{e^{\hbar \omega_0 / 2 k_B T} - 1} \right] \quad (5)$$

where  $\Gamma_0$  is the FWHM at 0 K and  $\omega_0$  corresponds to frequency at 0 K. For  $1333\text{ cm}^{-1}$  IR mode for CuPc on (001) Si substrate during heating procedure the parameter  $\Gamma_0$  is equal 9.608.

The dependence of FWHM ( $\Gamma$ ) as a function of temperature has not been fitted.

The linewidth of other modes also broadens with increasing temperature, but the sparse line shapes and low intensities of the peaks prevents accurate quantification of the temperature dependence of its FWHM.

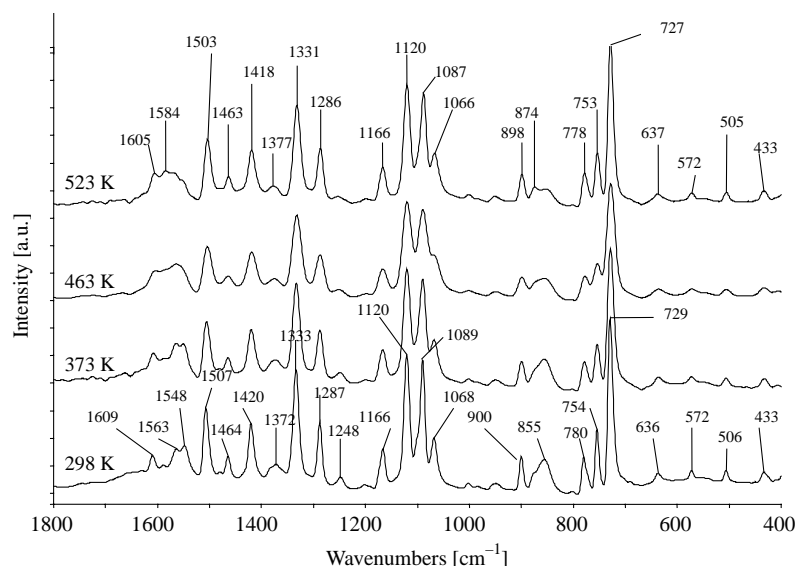


Fig. 6. The FT-IR absorption spectra of CuPc molecules in KBr at different temperatures.

The vibrational absorption spectra of CuPc in KBr pellets are presented in Fig. 6 in the range from 1800 to 400  $\text{cm}^{-1}$  at different temperatures. FT-IR absorption spectra do not change significantly with temperature below 270 K (Fig. 6). As it can be seen from our investigations the 1333  $\text{cm}^{-1}$  stretching vibrational mode observed in FT-IR absorption spectra (Fig. 6) and 1523  $\text{cm}^{-1}$  in Raman spectra (Fig. 2) are expected to be little affected by anharmonicity due to its large wavenumber value compared with thermal energies at these temperatures [19].

Similar dependencies of integral intensity and band position observed for Raman modes are also observed for FT-IR modes. The dependence of the integral intensity during heating process versus temperature for FT-IR mode 1333  $\text{cm}^{-1}$  is presented in Fig. 7. This dependence can be described by Eq. (2). We observed strong increase of integral intensity of vibration mode at 278 K and a weaker increase at

480 K. As in case of Raman modes the values of  $E^A$  and  $E^D$  energies have been also estimated. As it can be seen from Figs. 3a, b and 7, the order of these values for both, Raman scattering and FT-IR absorption investigations are comparable with typical values for inorganic crystalline materials. The obtained fitting parameters  $E^A$  and  $E^D$  suggest the existence of partial polycrystalline form [21–23].

The dependence of 1333  $\text{cm}^{-1}$  (RT) vibration frequency as a function of temperature during the heating process from 100 to 565 K is presented in Fig. 8. This dependence can be described by expression (3) [17]. The solid curves in Fig. 8 represent the fit to the data for CuPc layers on (001) Si substrate using Eq. (3). As it can be seen from Fig. 8, we observe anomalies, strong one at 278 K and very weak at 480 K. The observed changes of vibration frequency can be probably caused by the change of the molecular structure of CuPc to  $\alpha$ -form (278 K) and to  $\beta$ -form (480 K).

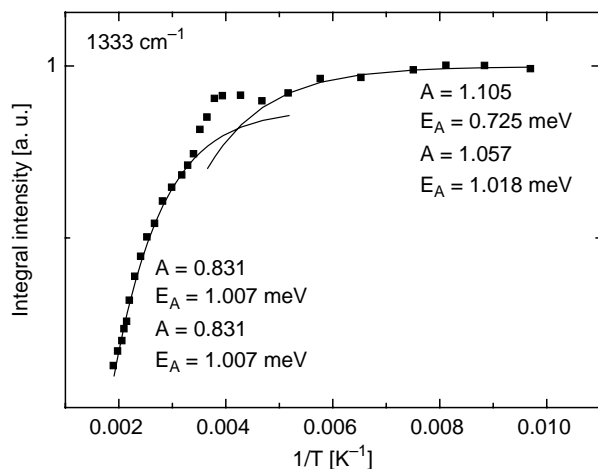


Fig. 7. The temperature dependence of the integral intensity of 1333  $\text{cm}^{-1}$  band during heating process. The solid curves represent the fit to the data using Eq. (2).

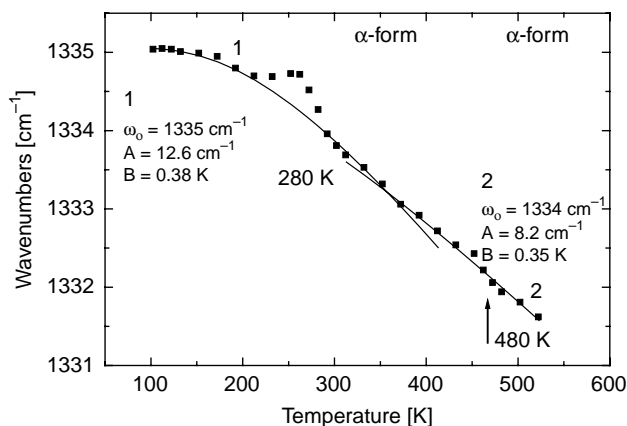


Fig. 8. The dependencies of FT-IR vibration mode position at 1333  $\text{cm}^{-1}$  (RT) of CuPc layer on (001) Si substrate as a function of temperature while heating from 100 to 565 K. The solid curves represents the fit to the data using Eq. (3).



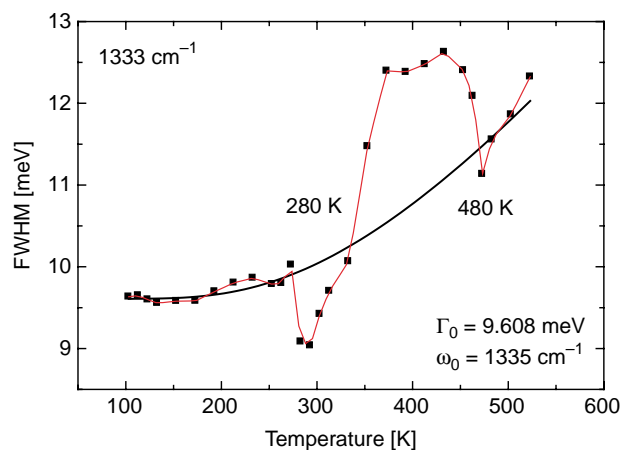


Fig. 9. The dependence of the Lorentzian broadening parameter  $\Gamma$  (FWHM) on the temperature for the  $1333\text{ cm}^{-1}$  vibration mode of CuPc. The solid curves represent the fit to the data using Eq. (5).

In Fig. 9 we present the dependence of the Lorentzian broadening parameter  $\Gamma$ , i.e. the FWHM on the temperature for the  $1333\text{ cm}^{-1}$  vibrational mode of CuPc. On this curve we can see two minima at 278 and 480 K. These changes can be attributed to the change of molecular form of CuPc structure. Thus, the temperature dependence of  $\Gamma$  for CuPc can be expressed by Eq. (4).

The obtained results from Raman scattering and FT-IR absorption experiments revealed the change of the integral intensity and peak position of  $1335$  and  $1523\text{ cm}^{-1}$  bands during heating and cooling process. The position of these bands and their integrated intensity show the local maxima at about 270 and 480 K. The observed feature can be probably connected with the change of molecular forms.

## 5. Conclusions

Raman scattering and FT-IR absorption measurements allowed us to determine the temperature dependence of vibrational modes of CuPc crystalline layers. From mentioned above studies we obtained the temperature dependencies of the integral intensity, band position and full width at half maximum of these modes. Some anomalies in temperature dependencies of integrated intensity and FWHM for modes observed in FT-IR absorption and Raman scattering spectra have been observed at 270 K (in FT-IR) and 480 K (in Raman and FT-IR) indicating some changes

of the structural forms, probably to  $\alpha$  and  $\beta$  form, respectively. The CuPc thin layers deposited on (001) Si substrates possess  $\alpha$ -form. With the increase temperature of the substrate above 480 K develop a preferred structural of the CuPc molecules of the  $\beta$ -form.

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