

Optical Absorption by Polarons in Rutile (TiO_2) Single Crystals

By

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The optical absorption in rutile single crystals doped with Nb and other impurities as well as partially reduced is investigated in the temperature range 10 to 900 °K. It is shown that the spectrum and the magnitude of the optical absorption by current carriers can be satisfactorily explained in terms of the small polaron theory. The oscillator strength for the absorption band studied as well as the polaron binding energy, the mean electron-phonon coupling constant, and the nearest neighbour overlap integral are estimated from the experimental data.

В широком интервале температур (10 до 900 °K) исследовано оптическое поглощение носителями тока в кристаллах рутила как частично восстановленных, так и легированных ниобием и другими примесями. Показано, что как характер спектра, так и величина поглощения удовлетворительно описываются теорией поляронов малого радиуса. Из экспериментальных данных оценены сила осциллятора исследованной полосы поглощения а также величина поляронного сдвига, средней константы электрон-фононного взаимодействия а также интеграла перекрытия между ближайшими соседями.

1. Introduction

The intraband absorption of light by current carriers is the source of valuable information on scattering mechanisms (from absorption spectrum) and on the effective mass of carriers (from reflection spectrum). Such investigations are especially interesting for strong electron-phonon interaction, and if one can expect a considerable polaron effect.

When the electron-phonon coupling is weak the absorption coefficient $\alpha(\omega)$ usually decreases continuously with frequency (e.g. for scattering by longitudinal optical phonons $\alpha(\omega) \sim \omega^{-5/2}$ [1]). In the case of large polarons there may be superimposed some peaks on this curve, corresponding to the internal structure of the polaron [2]. Finally, in the theory of small polarons the optical absorption spectrum has a resonance character [3 to 8]. In this last case the study of the absorption spectrum gives us an independent experimental method for the polaron detection in crystals, the estimation of the polaron binding energy, and the electron-phonon coupling constant. Moreover, as it is shown recently by Firsov [9], from the absorption spectra one can obtain information about the character of polaron motion in crystals. The absorption measurements must be carried out in the frequency range between the fundamental absorption edge and lattice absorption. The reason for this is that the frequency for the small polaron absorption maximum must be at least several times greater than the frequency of optical phonons.

In our recent papers [8, 10] the results of the measurement of the optical absorption in semiconducting crystals of rutile (TiO_2) have been presented

for partially reduced rutile as well as for Li- and P-doped samples. This material has been chosen for investigation because the experimental data on transport phenomena reveal that the current carriers in this case are probably small polarons [11, 12]. (This suggestion was confirmed later by theoretical analysis [13].

It was shown in [8] and [10] that the absorption spectrum in all conducting samples has resonance character. Neither the shape of the spectral dependence nor the position of maximum absorption (≈ 0.8 eV) depends on the nature of the donors. All experimental data show that this absorption is due to the interaction of light with current carriers.

It was concluded from the character of the absorption spectrum (broad peak) that this absorption is due to multiphonon processes which occur by interaction of light with polarons. According to theoretical investigations carried out by Kudinov and Firsov [8] on the optical absorption by small polarons there was established in the limiting case of narrow bands the resemblance with the theory of absorption by colour centers. The absorption mechanism is explained on the basis of the Frank-Condon principle. It was shown that the experimental data qualitatively agree with the theory of small polaron absorption.

For quantitative comparison with theory it was interesting to carry out measurements in the high-temperature range. This could not be done on samples studied in [8] because of the thermal instability of nonstoichiometric defects produced by heat treatment in vacuum (or in hydrogen), and of Li and P donors introduced by diffusion. In this paper we present and discuss optical absorption measurements in niobium-doped samples for temperatures up to 900 °K.

It was established that after a specific heat treatment the absorption spectra become more complex and show a new high-frequency maximum (near 1.2 eV). Similar phenomena were observed by Cronmeyer [14] in heavily reduced rutile crystals. Such changes in absorption spectra are also studied and discussed in this paper.

2. Experimental

Rutile single crystals used in this study were produced by the Verneuil technique. The specimens were cut from single crystals and reduced by heating in vacuum (or in hydrogen atmosphere) or doped with Li or P. The experimental procedure of reducing and doping with Li and P was described in [8]. The single crystals doped with Nb have been produced also by the Verneuil technique. At room temperature the conductivity of the Nb-doped samples was about $0.5 \Omega^{-1} \text{ cm}^{-1}$. — Before the measurements, these samples were annealed for several hours in air at 900 °C. The concentration of residual oxygen vacancies may be neglected after such treatment. Therefore, the optical and electrical properties of the samples studied are mainly due to the Nb donors.

The crystal plates used in our measurements were all cut in such a way that their faces were perpendicular to the c -axis of the crystal. Therefore, the electric vector of the light E was also perpendicular to the c -axis ($E \perp c$). The transmission spectra have been measured in the frequency range from 2000 to 11000 cm^{-1} using an UR-10 double-beam spectrometer. The reflection measurements show that the reflection coefficient of doped samples having a conductivity $\sigma_0 < 1 \Omega^{-1} \text{ cm}^{-1}$ agrees well with calculated values $R = \left(\frac{n_0 - 1}{n_0 + 1} \right)^2$, where

n_0 is the refraction index for the ordinary beam given for undoped crystals in [14]. The absorption coefficient dependence was calculated from the optical transmission data utilizing these values of R .

3. Experimental Results

The absorption coefficient α is given in Fig. 1 as function of the photon energy (in cm^{-1} and eV) for Nb-doped (curve 1) and for Li-doped material (curve 3) as well as for that one reduced in hydrogen (curve 2). All three curves are very similar. The absorption coefficient spectra consist of a single broad peak at about 6600 cm^{-1} (0.82 eV). It has been shown in [8] that for reduced samples as well as for Li- and P-doped ones the optical absorption in near infrared is a unique function of the static conductivity σ_0 . There is a simple relationship between the absorption coefficient maximum α_M and σ_0 . At 300°K it is

$$\frac{\alpha_M [\text{cm}^{-1}]}{\sigma_0 [\Omega^{-1} \text{cm}^{-1}]} = (5.3 \pm 0.5) \times 10^2 \Omega. \quad (1)$$

It has been assumed that this relationship holds also for Nb-doped samples. This proportionality between α_M and σ_0 exists in the conductivity range at least from 10^{-2} to $5 \times 10^{-1} \Omega^{-1} \text{cm}^{-1}$ (Fig. 2). With increasing temperature α_M decreases, σ_0 increases and, therefore, the ratio α_M/σ_0 decreases. At 700°K we have

$$\frac{\alpha_M [\text{cm}^{-1}]}{\sigma_0 [\Omega^{-1} \text{cm}^{-1}]} \approx 4 \times 10^2 \Omega. \quad (2)$$

For evaluating the absorption intensity (related to one carrier) and oscillator strength of the absorption band it was necessary to determine the density of current carriers. From this density we could also compute the conductivity mobility μ .¹⁾

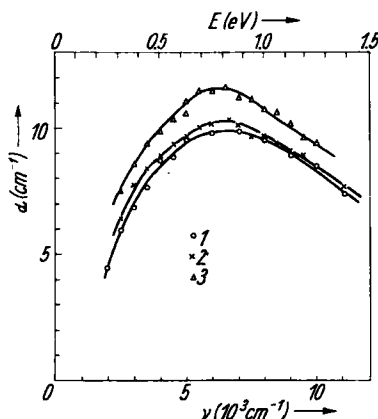


Fig. 1. Room temperature absorption spectra of Nb-doped (1), reduced (2), and Li-doped (3) rutile crystal. For curve (1) the values of α must be multiplied by 20

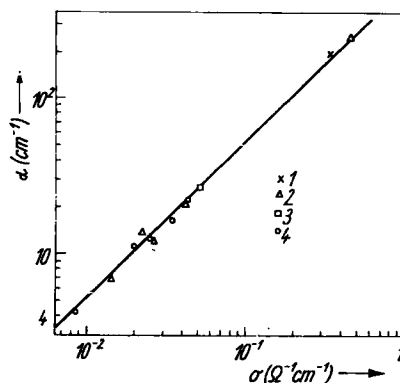


Fig. 2. Room temperature absorption coefficient in the absorption band maximum as a function of dc conductivity for samples with various donors. \times Nb-doped, \triangle reduced, \square Li-doped, \circ P-doped. The solid line has a slope of $\alpha/\sigma = 530 \Omega$

¹⁾ For polaron conduction mechanism the Hall mobility in general does not coincide with the conductivity mobility and the Hall coefficient is not a simple measure of the carrier density [13].

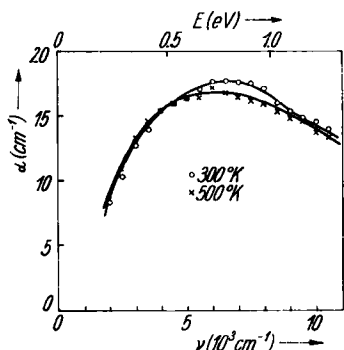
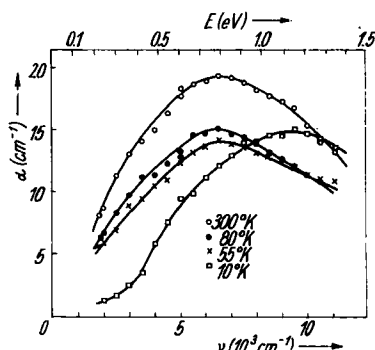


Fig. 3. Absorption spectra of Li-doped samples

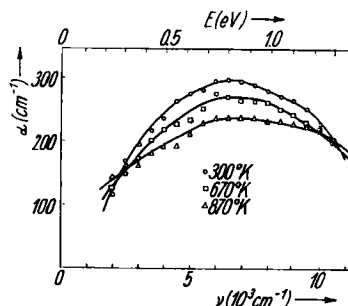
Fig. 4. Absorption of a vacuum-reduced sample of TiO_2 at 300, 80, 55, and 10 °K

In this work the density of carriers was determined from the donor density in Li-doped samples. It was supposed that at 300 °K the Li atoms are completely ionized. We believe that this assumption is fulfilled because the absorption intensity in Li-doped samples does not change by increasing the temperature from 300 to 500 °K (see Fig. 3). Apparently, the ionization energy of Li donors is very small.

The density of Li atoms was determined by flame photometry. The rutile specimen placed in a sealed capsule containing water was annealed for a long time at a temperature of about 150 to 200 °C. The change in sample conductivity and the Li content in the water was determined after annealing. By such procedure we could relate the carrier density to the sample conductivity and optical absorption. It was assumed for the calculation that n is equal to the density of Li atoms. It was found that $n = (1.1 \pm 0.2) \times 10^{16} \text{ cm}^{-3}$ corresponds to $\sigma_0 = 0.024 \Omega^{-1} \text{ cm}^{-1}$ and $\alpha_M = 13 \text{ cm}^{-1}$, i.e. the absorption maximum $\alpha_M = 1 \text{ cm}^{-1}$ corresponds to a carrier density $n = 8.6 \times 10^{16} \text{ cm}^{-3}$. The conductivity mobility determined from these data was found to be equal to $0.14 \pm 0.03 \text{ cm}^2/\text{Vs}$. This result must be referred to a current flow perpendicular to the c -axis of the crystal and agrees with the estimation from transport phenomena given in [13]. It must be noted that this value of the conductivity mobility agrees also with the Hall mobility at 300 °K [13, 15 to 17]. For increasing temperature the carrier density does not change in our case whereas the conductivity in this temperature range slightly increases. Therefore, such an estimation gives a conductivity mobility at 500 °K which differs from μ at 300 °K by not more than 10 to 20%. On the contrary, the extrapolation of the data given in [16] shows that the Hall mobility at 500 °K is several times smaller than its room temperature value because of decreasing Hall coefficient.

The temperature dependence of the low-temperature absorption spectra was studied in [8] on a reduced sample. It turned out that with decreasing temperature the intensity of the spectrum decreases. This is obviously caused by the decrease in the carrier density (Fig. 4). At a temperature of about 10 to 20 °K the peak at 6600 cm^{-1} (0.82 eV) "freezes out" and a new spectrum with a maximum near 1.18 eV appears, due probably to absorption by donors. At these temperatures, a sharp decrease in the conductivity takes place in rutile according to [17].

Fig. 5. Absorption spectra of a Nb-doped sample at 300, 670, and 870 °K (sample No. 16a)



Absorption measurements in the high temperature region (up to 900 °K) were carried out in this work. The results of these measurements for an Nb-doped sample are presented in Fig. 5. It may be seen that with increasing temperature the absorption peak decreases and the absorption band begins to broaden. We shall discuss these results in the next section.

The P-doped samples studied in [8] were annealed at 800 °C and under a pressure of phosphorus corresponding to 230 °C. After this treatment the crystals were heated in oxygen atmosphere at 750 °C. The absorption spectra of such samples are similar to those for reduced samples. However, after the temperature of phosphorus was raised up to 330 °C, the absorption spectra become more complex and show new high-frequency maxima.

Similar phenomena have been observed by Cronemeyer [14] after heavy reduction of rutile crystals in hydrogen. In his work for crystals having a conductivity of more than $0.33 \Omega^{-1} \text{ cm}^{-1}$ at room temperature composite spectra were obtained having pronounced maxima at 1.17 eV. This second maximum, however, was absent in samples with conductivity less than $0.25 \Omega^{-1} \text{ cm}^{-1}$. In such crystals the absorption spectra were similar to those ones presented in Fig. 1 of this paper.²⁾

Probably, this complication in the spectra is in both cases due to similar reasons. To clear up the nature of the high-frequency peak we have investigated the temperature dependence of the spectra in such "anomalous" samples. The measured data for sample No. 21 are shown in Fig. 6. The experimentally obtained dependence for the temperatures of 78, 300, and 600 °K are given as solid lines. The spectral curves for 78 °K as well as for 300 °K show an intensive peak at about 1.2 eV which is absent in a high-temperature curve (600 °K). The shape of this high-temperature spectrum is very similar to that of the spectra in Fig. 1 and 3.

It was suggested that the spectra obtained consist of two peaks. The first (low-frequency) peak is due to absorption by current carriers and the shape of this spectrum is similar to that of the "normal" samples (Fig. 1 and 3). The rest of the optical absorption is to be attributed to the high-frequency peak. The

²⁾ We failed to reproduce these results of Cronemeyer's work. For samples reduced in hydrogen atmosphere having at room temperature a conductivity of $\sigma_0 = 0.45 \Omega^{-1} \text{ cm}^{-1}$ the absorption spectra do not show the second peak. We believe that this discrepancy is due to a difference in the annealing and heat treatment used in [14] and in our work.

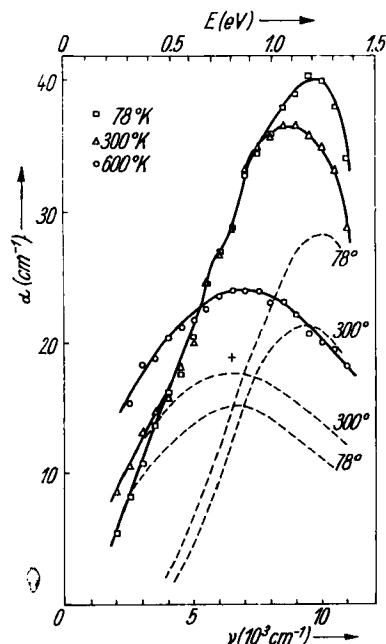


Fig. 6. Absorption spectra of sample No. 21 at temperatures of 78, 300, and 600 °K (solid lines). The dashed lines were calculated by dividing the absorption spectra obtained at 78 and 300 °K into two components (see the text). + magnitude of α_M computed from σ_0 by using equation (1)

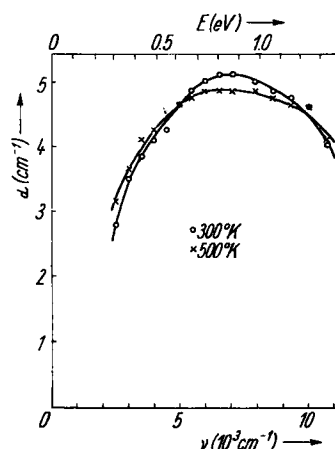


Fig. 7. Absorption spectra of a P-doped sample (No. 15)

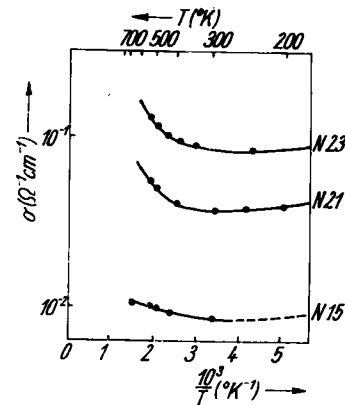


Fig. 8. Conductivity of samples No. 15, 21, and 23 in dependence on temperature

spectral dependence $\alpha(\nu)$ obtained for 78 and 300 °K was divided into two components according to this suggestion.³⁾ It is assumed by this separation that the absorption near 2500 cm^{-1} is due only to current carriers. The two pairs of spectral curves (two peaks at two temperatures) are shown in Fig. 6 as dashed lines. The value of α_M at 300 °K obtained from the above analysis (17.5 cm^{-1}) agrees satisfactorily with the value of 19 cm^{-1} calculated from conductivity by using (1). This confirmed the correctness of the above procedure of spectral component separation and interpretation of the low-frequency part of absorption.

For samples having no high-frequency peak in the spectra the intensity of absorption does not change with temperature (sample No. 15, Fig. 7). The temperature dependences of conductivity shown in Fig. 8 are different for sample No. 15 and for samples No. 21 and 23. (The high-frequency peak is present in

³⁾ This procedure is similar to that used in [14].

spectra of the two latter samples.) The increase in conductivity from 300 to 600 °K is much more pronounced in samples No. 21 and 23 than in sample No. 15.

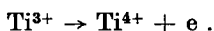
4. Discussion

The results obtained in this work confirm the interpretation of absorption in conducting rutile crystals as due to interaction of photons with current carriers. It should be noted that the absorption band in near infrared for reduced rutile was usually ascribed to the absorption by various defects. In particular the helium model of an oxygen vacancy capable of trapping two electrons (similar to an F'-centre) was discussed [14].

It is possible using this model to explain simultaneously the optical absorption and electric conductivity because an oxygen vacancy serves as a doubly ionizable donor. One can suppose that these donors are single ionized in a wide temperature range. Then the optical absorption due to ionization of the second electron from the vacancy should be proportional to the electric conductivity and may not be very strongly dependent on the temperature. In the case of another type of donors, namely interstitial ions of Ti^{3+} , the absorption coefficient may also be proportional to the conductivity. According to Blumenthal et al. [22] such defects are generated by reduction of TiO_2 :



The optical absorption may be due to transitions between 3d levels of Ti^{3+} ions⁴⁾ or due to photoionization of these ions:



However, in crystals of TiO_2 doped with Nb studied in this work the impurity atoms are placed in titanium sites in the state Nb^{4+} according to [21], i.e. their electron configuration is $4d^1$. At temperatures above 40 to 60 °K the Nb^{4+} ions lose their single d-electron and the donor absorption cannot be observed. (We exclude from discussion the transitions from internal shells.) As for the possible nonstoichiometric defects in the crystals investigated they should be annealed by the high temperature treatment before the measurements.

The parallel increase with temperature of the absorption in the 0.8 eV band and of the conductivity in samples with complex spectra seems to be very significant. If the temperature dependence of the conductivity in sample No.15 (see Fig. 8) is supposed to be due to a change in the mobility (all donors are ionized, absorption intensity does not depend on temperature), then the faster increase of σ_0 in samples No. 21 and 23 corresponds to an increase in the carrier density. The relative changes of the carrier density with temperature estimated from σ_0 and α_M are shown in Fig. 9. There is a satisfactory agreement between the data obtained by two independent methods. This confirms the interpretation of the optical absorption in the 0.8 eV band as due to current carriers. The high-frequency peak with maximum near 1.2 eV (at 78 °K) decreases with temperature simultaneously with increase of the 0.8 eV band. Therefore, this peak

⁴⁾ It should be noted, however, that the oscillator strength for such forbidden transitions is usually very small ($f < 10^{-3}$ to 10^{-4} [23]). This value is much smaller than f for the absorption band studied (see below in the text).

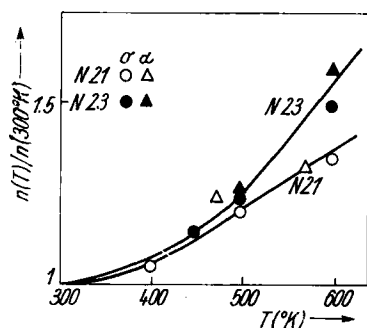


Fig. 9. Current carrier density in samples No. 21 and 23 calculated from changes of conductivity (σ) and optical absorption (α). The data are normalized to room temperature values

is apparently due to the optical absorption by non-ionized donors, the latter being generated in samples during the heat treatment described above.⁵⁾ The nature of these donors is still unknown. It may be pointed out that the high frequency peak in these samples is near the absorption peak in vacuum-reduced samples at helium temperature.

The possible mechanisms of the interaction of light with current carriers were analysed in [8] for weak electron-phonon coupling (intraband as well as interband transitions). It was shown that the properties of absorption spectra for rutile may be explained only taking into account strong electron-phonon interaction. The experimental data were consistently accounted for by small polaron theory. In the rest of this paper a qualitative comparison of the optical absorption in TiO_2 with the small polaron theory will be given.

The real part of the high-frequency conductivity of the small polaron theory is given by⁶⁾

$$\text{Re } \sigma(\omega) = \frac{1}{3} Z n_0 e^2 a_0^2 \left(\frac{I}{\hbar} \right)^2 \frac{1}{\hbar \omega} \sqrt{\frac{\pi \hbar^2}{16 E_a kT}} \exp \left[-\frac{\hbar^2 (\omega - \omega_M)^2}{16 E_a kT} \right], \quad (3)$$

where Z is the number of nearest neighbours, n_0 the density of current carriers (polarons), a_0 the lattice constant, I the nearest neighbour electronic overlap integral which determines the width of electronic band in the tight-binding approximation, $\hbar \omega_M = 4 E_a$, E_a the activation energy which determines the temperature dependence of the direct current mobility for $T \rightarrow \infty$. Expression (3) represents a Gaussian curve with a maximum at $\hbar \omega_M = 4 E_a$ and is valid for high temperatures (for $kT \gtrsim 1/2 \hbar \omega_0$ where $\hbar \omega_0$ means the effective energy of optical phonons with which electrons are coupled). Even in high-temperature range equation (3) is applicable only for frequencies

$$\omega \lesssim \omega_M \frac{2 kT}{\hbar \omega_0}.$$

On the high-frequency side of the maximum $\text{Re } \sigma(\omega)$ decreases more slowly as for a Gaussian curve [6].

In any case for temperatures exceeding 600 °K ($kT \approx 0.05$ eV) equation (3) may be used for an estimation of the absorption maximum because in TiO_2 it

⁵⁾ The appearance of non-ionized donors in heavily reduced rutile was observed recently by ESR measurements [27].

⁶⁾ See, e.g., equation (14) in [8]. Factor 1/3 in (14) was erroneously omitted.

is $\hbar \omega_0 \approx 0.1$ eV [24]. For this purpose it is convenient to express the parameters of expression (3) in terms of those ones determined directly from the experiment (σ_0 , ω_M).

For high temperatures

$$\sigma_0 = \frac{1}{3} Z n_0 e^2 \alpha_0^2 \left(\frac{I}{\hbar} \right)^2 \sqrt{\frac{\pi \hbar^2}{16 E_a (kT)^3}} \exp \left(-\frac{E_a}{kT} \right) \quad (4)$$

and

$$E_a = \frac{\hbar \omega_M}{4},$$

equations (3) and (4) give

$$\operatorname{Re} \sigma(\omega) \approx \sigma_0 e^{\hbar \omega_M / 4 kT} \frac{kT}{\hbar \omega} \exp \left[-\frac{\hbar^2 (\omega - \omega_M)^2}{16 E_a kT} \right], \quad (5)$$

i.e. for $\omega = \omega_M$

$$\operatorname{Re} \sigma(\omega_M) \approx \sigma_0 \frac{kT}{\hbar \omega_M} \exp \left(\frac{\hbar \omega_M}{4 kT} \right). \quad (5')$$

For the absorption coefficient $\alpha(\omega)$ we have the well-known expression

$$\alpha(\omega) = \frac{4\pi}{n c} \operatorname{Re} \sigma(\omega), \quad (6)$$

where $n = \sqrt{\epsilon_\infty}$ is the index of refraction.

For the absorption coefficient to conductivity σ_0 ratio (this value was determined from measurements) we have from (5) and (6)

$$\frac{\alpha(\omega_M)}{\sigma_0} = \frac{4\pi}{n c} \frac{kT}{\hbar \omega_M} \exp \left(\frac{\hbar \omega_M}{4 kT} \right). \quad (7)$$

For 700 °K ($kT \approx 0.06$ eV) and $\hbar \omega_M = 0.8$ eV from (7) we get $\alpha(\omega_M)/\sigma_0 = 3.7 \times 10^{-10}$ cgs units = 335 Ω being in satisfactory agreement with the experimental value (400 Ω).

As may be seen from equation (3) the optical absorption in the maximum should be proportional to $(T)^{-1/2}$, the band width should be proportional to $T^{1/2}$, i.e. the product of α_M and the band width is constant. Because of the large band width its accurate measurement is difficult whereas the value of α_M may be determined easily. For sample No. 16a doped with Nb (Fig. 5) α_M decreases from 275 cm^{-1} at $T_1 = 670$ °K to 235 cm^{-1} at $T_2 = 870$ °K, i.e. by a factor of 1.17 being close to $(T_2/T_1)^{1/2} = 1.14$.

It must be emphasized, however, that with increasing temperature when kT becomes compared with E_a , the thermal motion destroys the polarization well. Besides, the broadening of the absorption band changes also the character of the spectra. It may be expected according to [4] that for $kT \gtrsim 0.5 E_a$ the maximum on the absorption curve disappears and the absorption spectrum becomes similar to that of ordinary free carriers. In view of this it is interesting to note that current carrier absorption measurements in the intrinsic region (1200 to 1300 °K) revealed that absorption in the range from 3000 to 11000 cm^{-1} is nearly independent of frequency, and $\sigma(\omega)$ is close to σ_0 [18, 25]. Keeping in mind the above results and the fact that $\sigma(\omega_M)$ at 900 °K exceeds σ_0 according to our data only by the factor of 1.57) it is evident that both the character of

⁷⁾ At room temperature $\sigma(\omega_M)/\sigma_0 \approx 3.5$.

the spectrum and the magnitude of absorption in doped samples approach the results obtained for undoped samples in the intrinsic region.

To estimate the oscillator strength f for the absorption band investigated we use Smakula's formula usually used in the theory of colour centres:

$$n_0 f = A \frac{n}{(n^2 + 2)^2} \alpha_M (\text{cm}^{-1}) \Delta E (\text{eV}), \quad (8)$$

where n_0 is the density of absorption centres, n the index of refraction, and ΔE the band width. The numerical factor A depends on the shape of the band, being equal to 0.87×10^{17} for a Gaussian curve, and for a Lorentzian to 1.3×10^{17} [26]. By putting $A = 10^{17}$, $n = 2.5$ and using the results of absorption measurements in Li-doped samples we obtain $f = 0.055$. From the position of the absorption curve maximum (0.8 eV) we can estimate the polaron-binding energy E_p , i.e. the energy gain obtained by self-trapping of electrons in the crystal lattice, and the mean coupling constant $\bar{\gamma}$ ($E_p = \bar{\gamma} \hbar \omega_0$). Using the approximate expression $E_p \approx 1/2 \hbar \omega_M$ we have $E_p \approx 0.4 \text{ eV}$ and $\bar{\gamma} \approx 0.4$. This expression is correct if the dispersion of phonons is negligible. Therefore, the above estimation gives only the lower limit for E_p and $\bar{\gamma}$. For the nearest-neighbour overlap integral we get from (3) and the measured magnitude of maximum absorption the estimation $I \approx 0.1 \text{ eV}$.

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