

AN EXPERIMENTAL DETERMINATION OF THE LIGHT ABSORPTION COEFFICIENT IN SHOCK-COMPRESSED NaCl. THE ABSORPTION AND CONDUCTIVITY MECHANISM

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The absorption coefficients α for visible light in shock-compressed NaCl were measured experimentally. For $P = 465$ kbars and $T = 2550^\circ\text{K}$, $\alpha = 1.5 \text{ cm}^{-1}$. With increase of pressure and temperature α increases and for $P = 790$ kbars and $T = 4850^\circ\text{K}$, $\alpha = 10\text{--}12 \text{ cm}^{-1}$. The values of α at 4780 and 6250 Å are close to each other. The absorption coefficients found are about 100 times greater than those observed under normal conditions. A consideration of the experimental data and possible mechanisms of light absorption leads to the conclusion that in shock-compressed NaCl absorption and conductivity are due to free electrons. The free electron concentration and mobility are deduced from the magnitude of the absorption and conductivity coefficients in shock-compressed NaCl. A mechanism of the phenomenon is proposed according to which NaCl, which is initially a dielectric, is transformed by the shock-wave front into a semi-conducting state with donor levels. The concentration of donors generated by the shock-wave front during plastic deformation reaches 10^{19} cm^{-3} . Free carriers in the conduction band arise as a result of thermal excitation of electrons from the donor levels.

INTRODUCTION

UNDER ordinary conditions (normal pressure and temperature) ionic crystals (defined in the present paper only as halides of alkali metals) are dielectrics and transmit light in a sufficiently broad range of wavelengths from $\sim 0.2\text{--}0.3$ to $60\text{--}130 \mu$. Under these conditions, if the ionic crystals do not contain specially introduced impurities, the absorption coefficient α for visible light amounts approximately to $5 \times 10^{-2} \text{ cm}^{-1}$.

In investigations devoted to temperature measurements^[1] it was observed that as a result of shock compression the transparency of ionic crystals greatly decreases. This was observed earlier^[2] also for Plexiglas. A characteristic feature of the results obtained in the measurement of temperatures of shock-compressed ionic crystals is the increase in the radiation brightness with propagation of the shock wave through the investigated sample, until, starting with a certain thickness, the brightness becomes constant (see Fig. 1). In^[1] the increase in the glow brightness was connected, as in^[3], with the increase in the layer of material compressed by the shock wave, and with its transparency. By experimentally determining the dependence of the brightness on the time, and knowing the rate of propagation of the shock wave and the density of matter behind its front, we can

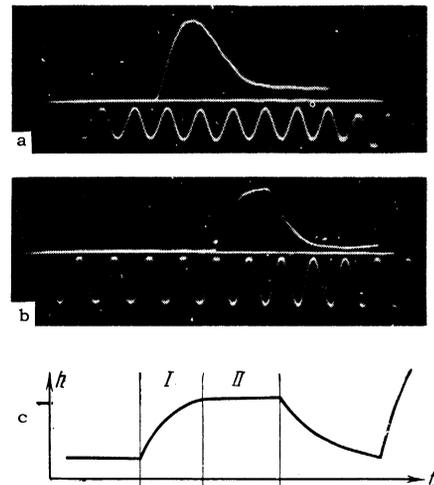


FIG. 1. Dependence of the radiation brightness on the time ($P = 615$ kbar); a - oscillogram obtained at $\lambda = 6250$ Å, b - the same at $\lambda = 4780$ Å, c - schematic representation of the oscillogram. The frequency of the timing sinusoid is 2 Mc.

find the coefficient of absorption of the compressed matter. The values obtained in this manner for NaCl turn out to be $\sim 1.5 \text{ cm}^{-1}$ at a pressure of 465 kbar ($T \approx 2550^\circ\text{K}$) and $10\text{--}12 \text{ cm}^{-1}$ for $P = 790$ kbar ($T \approx 4850^\circ\text{K}$). The values of the absorption coefficients, determined at wavelengths 4780 and 6250 Å, coincide within the limits of experimental accuracy. Under these conditions, the values of the absorption coefficients of shock-compressed

NaCl exceed by approximately a factor of 100 the values which are characteristic of normal conditions. They increase with increasing temperature. The present paper is devoted to an examination of the physical nature of this phenomenon and to the conclusions which can be drawn concerning the mechanism of light absorption and conductivity in shock-compressed ionic crystals.

The mechanism of absorption of light by shock-compressed gases was considered in detail by Zel'dovich, Raizer, et al (a detailed exposition of the results, with references to the original papers, is found in^[4]). Optical absorption in ionic crystals can occur both as a result of excitation of crystal-lattice vibrations (infrared absorption) and as a result of electron excitation. The following were considered: infrared absorption with account of the shift of the absorption band upon compression of the medium, absorption by free and bound electrons in an ideal crystal, absorption by color centers, and finally absorption by free electrons which are thermally "thrown" into the conduction band from the valence band and from donor levels (defects, impurities). Deferring the detailed exposition of the deductions of our analysis to Secs. 2 and 3, we shall mention the main conclusion that the absorption is determined by the free electrons. The most convincing evidence in favor of this is the weak dependence of the absorption coefficient on the wavelength. This result, together with the value of the absorption coefficient $\alpha \approx 1.5\text{--}12\text{ cm}^{-1}$ and its dependence on the temperature, indicates that the absorption is not connected with the photo-excitation of the electrons of the valence band.

It follows therefore that the free carriers appear in the conduction band as a result of thermal excitation. Regarding it as established that the absorption is determined by the free electrons in the conduction band, it is natural to treat also the conductivity of shock-compressed NaCl, measured in the work of Al'tshuler et al.,^[5] not as ionic but as electronic, due to the same free carriers¹⁾. We then have two independently measured quantities—the absorption coefficient α and the conductivity Σ , from which we can find (see Sec. 3) the electron mobility μ and the free-carrier concentration N_e . The electron-mobility values obtained for NaCl turn out to be close (taking into account their temperature dependence) to the experimental data obtained by others^[6,7] and calculated from the Ziman relation^[8] for scattering by optical lattice vibrations. The values thus obtained for

μ and N_e were used to analyze the possible mechanism of light absorption and the conductivity of shock-compressed ionic crystals.

The hypothesis,^[9,10] according to which the drawing together of the bands upon compression of the matter makes possible thermal transition of electrons from the valence band to the conduction band, does not allow us to describe the experimental values of the absorption coefficients obtained in the present paper, or the data^[5] on the conductivity of shock-compressed NaCl and its temperature dependence. A mechanism is proposed for the phenomenon, according to which the ionic crystal, which is initially a dielectric, is transformed as a result of plastic deformation on the front of the shock wave into the semiconducting state with donor levels, the thermal dissociation of which causes the appearance of the free electrons in the conduction band. Within the framework of the proposed mechanism of the phenomenon, it becomes possible to describe all the available experimental data.

1. EXPERIMENTAL RESULTS

In the earlier investigation^[1], when measuring the temperature of shock-compressed NaCl and KCl, we registered the radiation from the front of the shock wave. These investigations yielded numerous plots of the front brightness against the time at shock-wave intensities in the NaCl from 460 to 800 kbar. The experimental setup and the recording method are described in detail in^[1].

Data on the brightness of the front were obtained in two sections of the spectrum (at 4780 and 6250 Å). At a glow rise time of $\sim 5 \times 10^{-7}$ sec, the recording apparatus, the resolution of which was $\sim 5 \times 10^{-8}$ sec, provided reliable data on the time dependence of the front brightness. Characteristic oscillograms obtained in one of the experiments in the red and blue sections of the spectrum, as well as their schematic representation, are shown in Fig. 1. Whereas in^[1] principal attention was paid to the period of the maximum brightness, or in some cases to the period of constant brightness (see period II on Fig. 1c), we are now interested in period I, during which the brightness of the front increases as a result of an increase in the layer of material compressed by the shock wave.

The brightness of the front J is proportional to the emissivity of the layer of matter a , compressed by the shock wave

$$J = J_0 a, \quad (1)$$

where J_0 is the black-body brightness at a tempera-

¹⁾Some objections against the ionic mechanism of conduction are discussed in Sec. 2.

P, kbar	σ	D, km/sec	T, °K	α , cm ⁻¹		Σ , ohm ⁻¹ cm ⁻¹	μ , cm ² sec ⁻¹ V ⁻¹	N _e , cm ⁻³
				$\lambda=4780$ Å	$\lambda=6250$ Å			
276 *	1.50 *	6.18 *	1320 *	—	—	8.6 · 10 ⁻⁴ *	(3.2)	1.7 · 10 ¹⁵
433 *	1.62 *	7.22 *	2280 *	—	—	6.8 · 10 ⁻² *	(2.4)	1.8 · 10 ¹⁷
465	1.65	7.40	2550	1.5	1.5	(1.2 · 10 ⁻¹)	2.31	3.2 · 10 ¹⁷
500	1.67	7.59	2900	5	3.5	(2.1 · 10 ⁻¹)	1.97	6.6 · 10 ¹⁷
547 *	1.70 *	7.85 *	3400	8	7	4.1 · 10 ⁻¹ *	1.94	1.3 · 10 ¹⁸
615	1.75	8.13	3500	9	8	(4.7 · 10 ⁻¹)	1.93	1.5 · 10 ¹⁸
705	1.81	8.52	3900	12	10	(7.1 · 10 ⁻¹)	2.14	2.1 · 10 ¹⁸
790 *	1.85 *	8.91 *	4850	12	10	3.26 *	4.66	4.4 · 10 ¹⁸

*Data of [5].

ture T. Neglecting the front reflection coefficient, which, as indicated in [1], does not exceed in NaCl ~ 2% (at a shock-wave intensity of 400–800 kbar), and using for the transmissivity τ an expression derived from Bouguer's law, we can write for the absorptivity of a layer of thickness l

$$a^* = 1 - \tau = 1 - \exp(-\alpha l), \quad (2)$$

where α is the absorption coefficient.

For material in thermodynamic equilibrium²⁾, the emissivity and the absorptivity are equal ($a = a^*$), and relation (2) should describe the increase in the front brightness as the shock wave propagates through the material. This formula makes it also possible to determine from the experimental brightness-growth curves the absorption coefficient of the shock-compressed material. Knowing the brightness of the front at three successive instants of time, we can easily obtain from (1), (2), and the condition $a = a^*$ the following expression for the absorption coefficient, previously used by Model' [3]:

$$\alpha = \frac{1}{(D-U)\Delta t} \ln \frac{1 - J_1/J_2}{J_3/J_2 - 1}, \quad (3)$$

where J_1 , J_2 and J_3 are the brightnesses of the front at three successive instants of time; $\Delta t = t_2 - t_1 = t_3 - t_2$; D and U are the wave and mass velocities of the shock wave.

It must be stipulated that the time duration of the section of the brightness-growth curve, which is used to find the value of α , should be smaller than the time interval which separates the entrance of the shock wave and the rarefaction wave into the

investigated crystal. In the opposite case, if the layer of the compressed matter behind the front of the wave is still sufficiently transparent, at the instant of the arrival of the rarefaction wave on the boundary of the screen with the investigated sample, the character of the glow growth will change to such an extent that the brightness measured from this instant of time may even decrease. [1]

The values of the absorption coefficients obtained from formula (3) at wavelengths 6250 and 4780 Å, together with the other parameters characterizing the state of the NaCl behind the front of the shock wave, are listed in the Table. The velocity of the shock wave D was determined experimentally, [1] and the values of the pressure and of the degree of compression σ were found in the data of Al'tshuler et al., [5] who investigated the dynamic adiabat of NaCl in the pressure range under consideration. The temperatures listed in the Table correspond to the average values of the temperatures measured experimentally in [1]. The same Table gives the values of the conductivity as given by [5]. The quantities indicated in the brackets were obtained by interpolation.

2. POSSIBLE MECHANISM OF ABSORPTION OF LIGHT BY SHOCK-COMPRESSED MATTER

From the data given in the Table it follows that under the conditions in question the absorption coefficient of shock-compressed NaCl amounts approximately to 1.5–12 cm⁻¹. It increases with increasing pressure and temperature and has close values for different wavelengths.

One of the possible types of absorption of light in ionic crystals is absorption resulting from the excitation of crystal-lattice vibrations, namely infrared absorption. Under normal conditions ($\sigma = 1$ and $T \approx 300^\circ\text{K}$), the infrared-absorption band lies in a wavelength region on the order of several dozen microns (for NaCl the dispersion frequency is $\nu_0 \approx 4.9 \times 10^{12} \text{ sec}^{-1}$, and for CsBr $\nu_0 \approx 2.3 \times 10^{12} \text{ sec}^{-1}$). When the material is compressed, the frequency of the oscillations increases, and

²⁾In solid dielectrics, the time for establishment of thermodynamic equilibrium is determined by the phonon-phonon interaction and is equal to the ratio of the mean free path of the phonon ($\sim 10^7$ cm) to the speed of sound ($\sim 10^5$ cm/sec), that is, approximately 10^{-12} sec. The electron-phonon interaction relaxation time is even shorter and amounts to $\sim 10^{-14}$ sec. Thus, under our conditions, equilibrium is established in a layer of thickness of the order of $< 10^{-6}$ cm, and equilibrium states are registered at $\alpha = 1 - 10 \text{ cm}^{-1}$.

this leads to a shift in the infrared-absorption band into the region of shorter wavelengths. Let us assume for estimating purposes that the change in the dispersion frequency upon compression is equal to the change in the average frequency of the lattice vibrations.^[11] According to^[12], the expression for the average lattice vibration frequency at 0°K is

$$\nu^2 \sim \sigma^{2/3} \left(\frac{dP_x}{d\sigma} - \frac{2}{3} \frac{P_x}{\sigma} \right). \quad (4)$$

For an ion interaction potential at $T = 0$ in the form of the sum of the overlap energy and the Madelung attraction energy, the pressure $P_x(\sigma)$ is equal to (see, for example,^[5])

$$P_x = A \left[\sigma^{2/3} \exp \left\{ \frac{r_{0k}}{b} (1 - \sigma^{-1/3}) \right\} - \sigma^{4/3} \right]. \quad (5)$$

Here A and b are constants, r_{0k} is the interband distance at $T = 0$, and $P = 0$. After substituting (5) in (4) we get

$$\frac{\nu}{\nu_0} = \left[\frac{\frac{r_{0k}}{b} \exp \left\{ \frac{r_{0k}}{b} (1 - \sigma^{-1/3}) \right\} - 2\sigma}{r_{0k}/b - 2} \right]^{1/2} \quad (6)$$

Assuming for r_{0k}/b and ν_0 the value given in^[11], we find, for example, that $\nu = 8.6 \times 10^{12} \text{ sec}^{-1}$ for NaCl and $\nu = 5 \times 10^{12} \text{ sec}^{-1}$ for CsBr if $\sigma = 1.7$. These values are still much lower than the frequencies at which the measurements were made ($\nu_1 = 4.8 \times 10^{14}$ and $\nu_2 = 6.3 \times 10^{14} \text{ sec}^{-1}$). Even an account of the thermal expansion of the absorption band^[11,13,14] cannot explain the obtained experimental data. Special measurements of the absorption coefficients in shock compressed CsBr have shown that the value of α for this compound is even somewhat larger than for NaCl, whereas the crystal should not absorb any noticeable amount of light if the absorption were due to excitation of optical lattice vibrations.

The obtained values of α can likewise not be attributed to photo-excitation of the valence-band electrons. For the direct transition of electrons from the valence band to the conduction band, the optical width of the energy gap in NaCl should decrease from ~ 8 eV under normal conditions to ~ 2 eV behind the front of the shock wave. Even if the compression and heating in the shock wave were to cause the energy gap to decrease so much, a direct optical transition would lead to values $\alpha \approx 10^4 - 10^6 \text{ cm}^{-1}$, that is, to values which are $10^3 - 10^5$ larger than obtained in the experiment. We can apparently also not attribute the obtained data to absorption resulting from indirect optical transitions. Although the indirect optical transitions are indeed characterized by absorption coeffi-

icients of the order of $10 - 10^3 \text{ cm}^{-1}$,^[7] i.e., values close to the experimental ones, the dependence of the absorption coefficient on the wavelength in this case is still such that under our conditions, when the measurements are made at wavelengths of 4780 and 6250 Å, the values of α should differ strongly (see, for example,^[7]), whereas the experimental values (see the Table) are practically equal.

One more possible mechanism of light absorption in ionic crystals is absorption by color centers. In this case, however, the absorption coefficient should be strongly dependent on the wavelength, since the absorption band has a bell-shaped character. Thus, for NaCl under normal conditions $h\nu_{\text{max}} = 2.7$ eV, and the half-width of the absorption F band is ~ 0.35 eV. When the material is compressed (without heating), the maximum of the absorption band shifts towards the region of shorter wavelengths, and its half-width increases little.^[15,16] Absorption of light by color centers can become comparable with the measured absorption if the concentration of the centers reaches $N_F \approx 10^{17} - 10^{18} \text{ cm}^{-3}$. The NaCl single crystals used by us, which were 8 cm thick, transmitted $\geq 80\%$ of the incident light (with account of reflection on both faces). This yields, according to the Smakula formula, $N_F \approx 10^{14} \text{ cm}^{-3}$, if the absorption is due entirely to F centers. Thus, we can speak of this light-absorption mechanism only if the color-center concentration increases sharply on the front of the shock wave. We shall return to this question in Sec. 4.

In shock-compressed matter the temperature is sufficiently high, and some number of electrons can be thrown from the valence band into the conduction band, and also from the donor levels, if the crystal contains defects or impurities on which electrons are localized. Disregarding for the time being the possible sources of free electrons, we note that such a mechanism leads to the appearance of free carriers which, in turn, can cause as a result of intraband transitions absorption of light.

Absorption by free carriers can be regarded within the framework of classical electromagnetic theory, according to which (the Drude-Zener relation) the absorption coefficient is proportional to the concentration of the free carriers and to the square of the wavelength λ . In this case with increasing pressure in the shock wave, and thus also with increasing temperature, an increase should take place in the concentration of the free carriers and of the absorption coefficient. As can be seen from the data of the Table, in a definite range of

pressures this is indeed the case. The absorption coefficients measured at $\lambda = 6250 \text{ \AA}$ are approximately equal to the values of α at $\lambda = 4780 \text{ \AA}$, whereas according to the Drude-Zener relation they should exceed the former by a factor 1.7.

We must bear in mind, however, the approximate character of this relation and the fact that an error by a factor of 1.5–2 still lies within the limits of accuracy with which we can determine the absorption coefficients, so that this disparity is not decisive.

Bearing in mind the weak dependence of the absorption coefficient on the wavelength and its explicit dependence on the temperature, it is most probable that the latter mechanism (absorption by free electrons which are thermally thrown into the conduction band from the lower lying levels) is decisive in this phenomenon. Within the framework of these concepts it is also natural to treat the conductivity, measured in shock-compressed NaCl^[5] as being electronic, determined by the same free carriers.

Al'tshuler et al reached a different conclusion.^[5] Having determined the temperature dependence of the conductivity experimentally, they found from the expression $\Sigma \sim \exp(-W_u/kT)$ an activation energy $W_u = 1.2 \text{ eV}$, and, judging from its magnitude, they concluded that the conductivity is ionic in character. We recall that under normal conditions $W_u = 1.87 \text{ eV}$ for NaCl, that is, it is 1.5 times larger than that measured in^[5]. When the material is compressed, the activation, which characterizes the ionic conductivity, should increase because the ions come closer together and the repulsion forces increase as a result.^[4] Frenkel^[17] and Mott and Gurney^[18] took into account small changes in the interionic distance by means of the pre-exponential term. At the appreciable density changes which are realized behind the shock-wave front, this can no longer be done and the growth of the argument of the exponential, that is, of the activation energy, must be taken into account. This is also borne out by the results of the experimental investigations.^[19-21]

It was established in the two latter investigations that the activation energy of self-diffusion increases with increasing pressure in proportion to the melting temperature. According to^[1], the melting temperature of NaCl increases like $\sim \sigma^2$. Assuming such a dependence, we find that the activation energy of the ionic conductivity increases from 1.87 eV under normal conditions to $\sim 5 \text{ eV}$ after compression by a factor 1.7. This is four times the experimentally measured^[5] activation energy. Objections to the ionic mechanism of conductivity

were raised also by Alder.^[10] He believes that the ionic conductivity cannot explain the result obtained in^[5], inasmuch as the NaCl is in the solid phase in the pressure range in question, and the conductivity of this phase should be sufficiently low. Taking into account the foregoing, there is every reason for assuming that the conductivity of shock-compressed NaCl has not an ionic but an electronic character, due to the free carriers.

3. DETERMINATION OF THE MOBILITY AND CONCENTRATION OF THE FREE ELECTRONS FROM THE EXPERIMENTALLY MEASURED ABSORPTION COEFFICIENT AND CONDUCTIVITY

Having two independently measured quantities—the absorption coefficient α and the conductivity Σ —and assuming that both are determined by the free carriers, we can find the mobility μ and the concentration N_e of the free electrons. Measurement of one of these quantities, say the conductivity, makes it possible to find only the product of the carrier density by their mobility, since

$$\Sigma = N_e \mu e \quad (7)$$

(e is the electron charge). To determine them separately, it is customary to measure in addition to the conductivity also the Hall coefficient R . The product $R\Sigma = \mu$ gives the mobility. For this purpose, measurement of the absorption coefficient is equivalent to measurement of the Hall coefficient.

Within the framework of the classical theory, the coefficient of absorption is connected with the concentration of the free carriers, the frequency ν of the incident light, and the damping parameter q (the frequency of collisions between the electron and ions of the lattice) by the Drude-Zener relation

$$\alpha = \frac{2N_e e^2}{ncm} \frac{q}{\nu^2 + q^2}. \quad (8)$$

Here n is the refractive index, c the speed of light, and m the mass of the electron. The damping parameter q is connected with the mobility by the relation

$$\mu = e / 2\pi m q. \quad (9)$$

From (7), (8), and (9) we easily obtain

$$q = \nu (4\pi \Sigma / anc - 1)^{-1/2}. \quad (10)$$

Relations (7)–(10) enable us to find from the experimentally measured conductivity and the absorption coefficient the damping parameter q , the mobility, and the concentration of the free carriers. The determination of the values of μ and N_e , unlike q , is connected with some assumption concerning

the effective mass m^* of the electron. In this paper the effective mass of the electron was assumed equal to the mass of the free electron m , which in accordance with^[18] is approximately valid for alkali-halide crystals. The value of the refractive index in compressed NaCl was found from the relation $n = [1 + (\epsilon_\infty - 1)\delta]^{1/2}$, where ϵ_∞ is the high-frequency dielectric constant under normal conditions. Measurements made for shock-compressed water^[22] and several other substances by an analogous method have shown that this relation describes the experimental data obtained under our conditions with an accuracy of the order of 10–15%.

The values of the mobility and free-electron concentration, determined from the values of α (at $\nu = 4.8 \times 10^{14} \text{ sec}^{-1}$) and Σ by the method considered here, and listed in the Table, are plotted in Fig. 2 against the measured temperature^[1] of shock-compressed NaCl. It is seen from Fig. 2 that the obtained mobilities at temperatures 2500–3900°K lie in the interval $700\text{--}570 \text{ cm}^3/2\text{-g}^{-1/2}$ or $2.3\text{--}1.3 \text{ cm}^2\text{-sec}^{-1}\text{-V}^{-1}$. It is of interest to compare the obtained values with those by others. Pekar^[23] cites data by Evans,^[6] according to whom the upper limit of the carrier mobility in NaCl at room temperature is $8.3 \text{ cm}^2\text{-sec}^{-1}\text{-V}^{-1}$. At $T = 84^\circ\text{K}$, according to Bube,^[7] $\mu = 250 \text{ cm}^2\text{-sec}^{-1}\text{-V}^{-1}$. Recalculation of this quantity to $T = 300^\circ\text{K}$ by means of the Froehlich formula $\mu \sim (e^\Theta/T - 1)$, where Θ is the Debye temperature, equal to 373°K for NaCl, yields $\mu = 7.6 \text{ cm}^2\text{-sec}^{-1}\text{-V}^{-1}$, which is very close to the value given by Evans. These quantities are represented in Fig. 2 by the point at $T = 300^\circ\text{K}$.

In ionic crystals, the dominating scattering is that of electrons by optical lattice vibrations. According to Ziman^[8] we have for this case

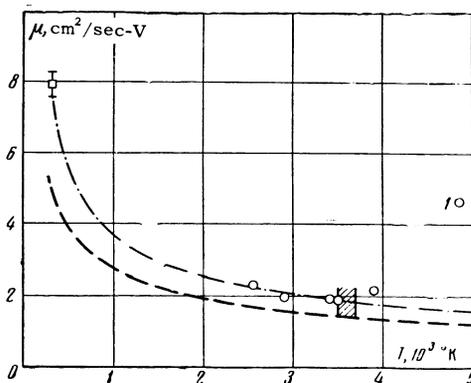


FIG. 2. Dependence of the free-carrier mobility on the temperature: \square – experiment^[6,7], \circ – our experiments, dashed line – calculation according to (11) with $C_0 = 0.259$, dash-dot line – calculation according to (11) with $C_0 = 0.20$. The melting region is shaded.^[1]

$$\mu \approx \frac{3}{\pi^{3/2} 2^{3/2}} \frac{\hbar^2}{em^{3/2}C_0} \frac{1}{(kT)^{1/2}}, \quad (11)$$

where $C_0 = 1/\epsilon_\infty - 1/\epsilon_0$, and ϵ_0 is the static dielectric constant. A plot of $\mu(T)$ is given by (11), with $C_0 = 0.259$ (corresponding to the values of ϵ_∞ and ϵ_0 under normal conditions) is shown also in Fig. 2 (dashed line). At $T = 300^\circ\text{K}$ we have $\mu \approx 5.4 \text{ cm}^2\text{-sec}^{-1}\text{-V}^{-1}$ which is close to the values of Evans and Bube. In our range of temperatures, the difference is also small. A satisfactory description of the obtained values of the mobility in the temperature interval from 2500 to 3900°K is attained at $C_0 = 0.20$ (see dash-dot line in Fig. 2)³⁾ Sufficiently good agreement between the obtained values of the mobility and the data by others^[6,7] (with account of the temperature dependence of μ) and the values calculated from (11) again favors the proposed mechanism of the phenomenon, whereby both the absorption of light by the shock-compressed matter and its conductivity are determined by the free electrons which are thermally “thrown into” the conduction band.

4. SOURCES OF FREE ELECTRONS AND MECHANISM OF LIGHT ABSORPTION AND CONDUCTIVITY IN SHOCK-COMPRESSED NaCl

In view of the lack of previous investigations of the transparency of shock-compressed condensed substances, we shall use for our further analysis the results of investigations of the conductivity behind the front of a shock wave. Alder and Christian^[26] investigated the conductivity of CsI, I_2 , red phosphorus, LiAlH_4 , NaCl, and teflon at shock-wave pressures of 50–250 kbar. On the basis of the fact that in the first four substances the resistance behind the wave front decreased by an approximate factor of 10^6 , they concluded that these substances go over into the metallic state, that is, that the conduction band overlaps the valence band. Investigations of the conductivities of I_2 , P,^[27] LiAlH_4 , and LiH,^[28] made under static conditions in the same and an even broader range of pressures, did not confirm this conclusion, although at higher pressures this may occur.^[29]

³⁾Strictly speaking, C_0 is a function of the density and of the temperature. Compression and heating on the front of the shock waves causes ϵ_∞ to increase^[22]. The joint influence of both factors on ϵ_0 has not been investigated. Compression leads to a decrease in ϵ_0 ^[24]; heating may produce the opposite effect.^[25] In the rather narrow compression interval considered here ($\sigma = 1.5 - 1.85$), we have taken as a first approximation $C_0 = \text{const}$. The non-fitting value of μ at $T = 4850^\circ\text{K}$ will be considered in Sec. 4.

Thus the situation in the experiments of Alder and Christian^[26] might have involved only the thermal overlap of the valence and conduction bands. A similar conclusion was reached by Tsukerman, Brish, and Tarasov,^[9] who investigated the conductivity of paraffin and Plexiglas, and subsequently also by Alder himself in his review paper.^[10]

The conductivity of shock-compressed NaCl was investigated in detail by Al'tshuler et al.^[5] This investigation has an advantage over those of Tsukerman et al.^[9] and Alder and Christian,^[26] since it included an examination, for the first time under shock-compression conditions, of the temperature dependence of the conductivity, thus making it possible to determine the activation energy. The authors of that paper, as indicated, concluded that the conductivity of NaCl is ionic.

We must stipulate, however, that the cited papers^[9,10,5] contain no direct proof that either of the conduction mechanisms, ionic or electronic, is to be preferred. Alder^[10] reserves the decision until the Hall coefficient is measured. The measurements made of the absorption coefficient permitted a choice to be made between these two mechanisms and to conclude that the conductivity and the absorption of light are due to the free electrons, thermally "thrown" into the conduction band. Examining from this point of view the results of Al'tshuler et al., we can obtain the width of the thermal gap. A plot of $\Sigma(1/T)$ is shown in Fig. 3. The experimental values of the conductivity were taken from^[5], and those of the temperatures from^[1]. For the high-temperature region ($T > 1300^\circ\text{K}$) the width of the energy gap, determined in accordance with the expression $\Sigma \sim \exp(-W/2kT)$ is ~ 2.4 eV. Using this value for the energy gap and the values obtained above for

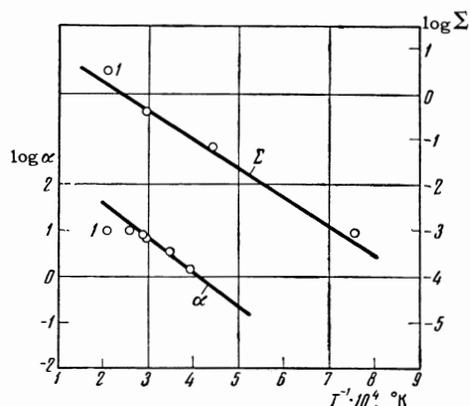


FIG. 3. Dependence of the conductivity Σ and the absorption coefficient α on the temperature. Points — experiment, continuous curve — calculations based on (7) — (9), (11), and (13).

the electron mobilities (see the Table and Fig. 2), we can check whether the valence band is the source of these free electrons which determine the conductivity and the absorptivity of the compressed matter.

The concentration of the free electrons, thermally excited from the valence band, is found from the relation

$$N_e = 2(2\pi mkT / h^2)^{3/2} e^{-W/2kT}. \quad (12)$$

For the state with $P = 547$ kbar and $T = 3400^\circ\text{K}$ at $W = 2.4$ eV we obtain $N_e = 1.7 \times 10^{19} \text{ cm}^{-3}$. Such a concentration of free electrons at a mobility $\mu \approx 2 \text{ cm}^2\text{-sec}^{-1}\text{-V}^{-1}$ (see Fig. 2) leads according to (7) and (8) to values approximately 13 times larger than the experimental ones for the conductivity and the absorption coefficient. This difference is beyond the experimental errors, at least for the absorption coefficient. To satisfy the experimental values of Σ and α in this state, the energy gap between the conduction and valence bands should be ~ 4 eV. The widths obtained in similar fashion for the energy gap for the states with $T = 2550$ and 4850°K are respectively ~ 3.3 and ~ 5 eV. The difference between the value $W = 2.4$ eV, obtained according to^[5] from the slope of the plot of $\log \Sigma(1/T)$, and the values $W \approx 3.3\text{--}5$ eV which are necessary within the framework of the considered hypothesis for reconciliation with the absolute values of Σ and α , are in our opinion the decisive objection against assuming that the source of the free electrons under these conditions is the valence band.⁴⁾ No change in the electron mobility can satisfy simultaneously the available experimental values of the conductivity and absorption coefficient. The change in the effective mass of the electron necessary for this is likewise unjustifiably large.

The foregoing analysis has led us to the conclusion that under the conditions in question the source of the free electrons is the donor levels which are located ~ 2.4 eV from the bottom of the conduction band. The necessary concentration of the donors can be obtained by assuming that the acceptor concentration $N_a = 0$, and using the relation⁵⁾

$$N_e = N_D^{1/2} (2\pi mkT / h^2)^{3/4} e^{-W/2kT}. \quad (13)$$

⁴⁾In the region of higher temperatures it is natural to expect this mechanism to be precisely the predominating one.

⁵⁾Estimates according to^[8,30] have shown that under the conditions in question in the case of NaCl we are not dealing with strong-coupling polarons^[23,30] but with the conduction electrons of the ordinary band theory.

Substituting here the value $N_e \approx 1.3 \times 10^{18} \text{ cm}^{-3}$ obtained above (for $\sigma = 1.7$ and $T = 3400^\circ\text{K}$) and $W = 2.4 \text{ eV}$, we find that the necessary donor concentration is $N_D \approx 1.6 \times 10^{19} \text{ cm}^{-3}$. This is approximately 10^5 times larger than the concentration of defects (for example, color centers; see Sec. 2), which is characteristic of ionic crystals under ordinary conditions. It follows therefore that the shock wave is a powerful generator of defects on which electrons are localized.

The possibility of the appearance of such a large number of defects is perfectly realistic. Thus, according to estimates by Van Bueren and Kanzaki,^[31] based on experimental data, the number of Schottky defects produced in ionic crystals after 10–35% plastic deformation amounts to 10^{18} – 10^{19} cm^{-3} . In many papers (see, for example,^[32]) it was shown that plastic deformation leads to the formation of F centers.

The foregoing analysis allows us to visualize the following mechanism for the phenomenon. When the shock wave propagates through the ionic crystal, dislocations are created on its front as a result of plastic deformation (in the region of non-hydrostatic compression), and their interaction leads to the formation of point defects on which electrons are localized. These defects (most likely color centers) serve as donors, which dissociate thermally in the shock-heated material, thus causing the appearance of free electrons in the conduction band. Thus, an ionic crystal, which is initially a dielectric, is converted by the shock-wave front into a semiconductor with donor levels whose concentration reaches ⁶⁾ 10^{19} cm^{-3} . The energy gap between the donor levels and the conduction band amounts to $\sim 2.4 \text{ eV}$ for NaCl.

Assuming a donor concentration $1.6 \times 10^{19} \text{ cm}^{-3}$, a thermal dissociation energy $W = 2.4 \text{ eV}$, and a parameter $C_0 = (1/\epsilon_\infty - 1/\epsilon_0) = 0.2$, we calculated the concentration of the free electrons using (13), the electron mobility from (11), the absorption coefficient at $\nu = 4.8 \times 10^{14} \text{ sec}^{-1}$ from (8) and (9), and the conductivity from (7). The results are compared with the experimental values on Figs. 2 and 3. As can be seen from the figures, the experimental data on the conductivity, absorption coefficient, and mobility fit quite well. The compared quantities differ nowhere by more than a factor of 1.5, which is within the experimental accuracy. An exception are the data at $P = 790 \text{ kbar}$ and $T = 4350^\circ\text{K}$ (point 1 on Figs. 2 and 3), where the calculated absorption coefficient exceeds the experimental one by approximately 3.5 times, and the calculated conductivity is smaller than the ex-

perimental value by the same factor.

We recall that the value of the electron mobility obtained from the experimental data for this state differs from the calculated mobility by approximately a factor of three (see Fig. 2). This may be due to the decrease in ϵ_0 as NaCl goes over into the liquid state (see Fig. 2), which leads to an increase in the mobility and in turn to a decrease in the absorption coefficient and an increase in the conductivity.

This difference, however, lies on the borderline of the experimental error, so that a more detailed examination and further experiments are necessary. In light of the proposed picture, there should be superimposed on the absorption by the free carriers also the absorption due to the photo-excitation of electrons localized on the defects. The concentration of the defects is sufficiently large, and the contribution from the absorption, resulting from the optical excitation, can be noticeable. The maximum of the photo-absorption band should lie at energies $> 2.4 \text{ eV}$, since the optical gap is wider than the thermal one (see, for example,^[18]). Check measurements (at $P = 547 \text{ kbar}$) have shown that at $\lambda = 4000$ and 4250 \AA the values of the absorption coefficient remain close to their values at $\lambda = 4780$ and 6250 \AA . This means that the absorption band lies at still higher energies ($h\nu_m > 3.1 \text{ eV}$). If we assume that we are dealing with F centers, this can be expected, since under normal conditions for NaCl the maximum of the band lies at 2.7 eV . Compression by a factor 1.7 should, according to^[15,16] lead to a shift of the maximum of the absorption band into the region of still higher energies $\sim 4.3 \text{ eV}$.

In conclusion we wish to call attention to one circumstance. From the experiments of Drickamer^[33] it is known that the polymorphic transition in KCl under static application of pressure occurs within times on the order of several dozen seconds, whereas under dynamic conditions the same transition, as follows from experiments of Al'tshuler et al.,^[34] occurs within a time on the order of 10^{-7} sec , in spite of the fact that the temperatures in the compared cases differ only by 30 – 40° . Such a large difference in the times may be due to the occurrence of a large number of defects on the front of the shock wave, accelerating the phase-transformation process. This hypothesis agrees with the notions of Alder,^[10] who relates the decrease in the time of the polymorphic transition under dynamic compression with shear deformations in the front of the shock wave.

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⁶⁾The acceptor levels can be considered analogously.

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