NONEQUILIBRIUM RADIATION FROM SHOCK COMPRESSED IONIC CRYSTALS AT $T > 1\,eV$. II

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The kinetics of electron transfer to the conductivity band behind the density discontinuity in the front of a shock wave is considered. It is shown that due to the finite time of the process, the radiation from the deep layers of matter, in which temperature equilibrium between the electrons and lattice is established, is screened by the "cold" electrons. A semiquantitative theory is proposed to explain the experimental fact that the temperature measured by an optical technique in alkali halide salts is smaller than that calculated by means of the equation of state. Agreement between theory and experiment is observed in the temperature range between 3×10^3 and $5 \times 10^{4\circ}$ K. Qualitatively it also explains the anomalously high temperature produced in shock compression of ionic crystals at about $2500°$ K.

INTRODUCTION

MEASUREMENTS of the temperature behind the front of a powerful shock wave in crystals of alkali-halide salts[1] have shown that, starting with $T \approx 10^{4\circ}$ K, for example for CsBr, a systematic lag is observed between the optically-measured temperature and the reasonable estimates that take into account, in particular, the influence of the melting of the crystal and the specific heat of the electrons excited in the conduction band[2]. In CsBr, the observed radiation is weaker than the calculated one by a factor of 60 at P = 5 Mbar.

The present article is devoted to a possible explanation of this effect by a detailed analysis of the kinetics of electron excitation. The developed theory is applicable for the explanation of the experimental results obtained in[1], for five ionic crystals—CsBr, KCl, NaCl, KBr, and LiF. It agrees with the experimentally measured temperatures on the shock-wave front in the region $(3-50) \times 10^{3}°$ K[2], and is logically connected with the mechanism of the appearance of the electrons in the conduction band of the crystal when the latter is shock compressed[3]. In addition, this theory explains qualitatively the anomalously high temperature in the shock compression of the crystals under consideration in the region of $2500°$ K and below[4].

THEORY

When the crystal is heated to the rated temperature, on the order of several electron volts, a noticeable transfer of electrons should take place at equilibrium from the filled valence band to the upper conduction band. The energy gap between these bands amounts to Q = 6—11 eV in alkali-halide crystals. Therefore a direct transfer of an electron by collision with a phonon is not very probable.

When electrons interact with phonons, they acquire and give up energy in small batches. When electrons collide with atoms or ions, this follows directly from the large mass ratio M/m_e. Inasmuch as phonons constitute a description of collective motions of heavy nuclei, it is clear that this conclusion can be trans-

ferred also to electron-phonon interactions. An electron that has accumulated sufficient energy by multiple collisions with phonons, causes another electron to be transferred to the conduction band. In such a situation, we can expect that after a relatively long period of time the temperature of the electrons e⁻ (and of the holes e⁺, to which all this applies to an equal degree) will be determined by the thermal balance, i.e., by the equality of the rate of transfer of energy from the phonons and of loss of energy to the transfer. Only after the transfer approaches the state of thermodynamic equilibrium do the energy losses to transfer turn out to be offset by the inverse processes $2e^- + e^+ = e^-$ and $2e^+ + e^- = e^+$, and the electrons and holes enter in a thermal equilibrium with the lattice.

The observed temperature corresponds to an optical thickness

$$L = \int_0^l \alpha \, dl = 1,$$

where α is the absorption coefficient and l is measured from the front of the shock wave[1]. If L = 1 is reached in a zone in which the transfer of the electrons still continues, then the measured temperature will be that of the electrons, i.e., a much lower value than the temperature of the lattice on the wave front or the equilibrium final calculated temperature. It is important here that one measure the radiation in the optical range, which depends on the transitions of the electrons inside the conduction band or on the transitions of the holes inside the valence band. Such a radiation characterizes the kinetic temperature of the electrons and of the holes, which is approximately constant for a relatively long time, during which the concentration of e⁻ and e⁺ changes in a wide range. In the corresponding zone, the concentration of e⁺ and e⁻ increases exponentially with increasing distance from the front to the interior of the compressed substance. In particular, it is curious that the distance between the wave and the

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[1]The thickness of the shock-wave front, i.e., the distance over which the crystal lattice is heated as a result of viscosity and thermal conductivity to a temperature Θ, is neglected.

effective radiating layer depends (logarithmically) on the initial concentation of e^+ and e^- on the front of the wave, but the observed temperature does not. We present below a semiquantitative calculation and a selection of parameters that make it possible to reconcile the proposed hypothesis with the observations.

Let us set up the equations[2]. By n we mean the concentration of the electrons in the conduction band; the concentration of the holes in the valence band is also equal to n. The rate of ionization via the reaction $e^- = 2e^- + e^+$ will be denoted $c_1 n$, and the corresponding rate for the reaction $e^+ = 2e^+ + e^-$ will be denoted by $c_2 n$; taken together, $(c_1 + c_2) n = cn$. In accordance with the principle of detailed balancing, we propose that the inverse recombination process occurs fundamentally via triple collisions; its rate is fn^3, so that

$$\frac{dn}{dt} = cn - fn^2. \tag{1}$$

The connection between f and c is determined by the fact that dn/dt = 0 when $n = n_{eq}(T)$, where n_{eq} is the equilibrium concentration for the given electron temperature T,

$$n_{eq} = 2\left(\frac{mkT}{2\pi\hbar^2}\right)^{3/2} e^{-Q/2kT} = n_0\left(\frac{T}{\Theta}\right)^{3/2} e^{-Q/2kT},$$
$$n_0 = 2(mk\Theta/2\pi\hbar^2)^{3/2}. \tag{2}$$

It is assumed that exchange of energy between e^+ and e^- is a fast process. The electrons and holes have a Boltzmann distribution, i.e., they have a definite temperature T, which differs from the lattice temperature Θ. We should expect a relation $c = \text{const} \cdot T^\beta e^{-Q/kT}$, and accordingly a weak (not exponential) dependence of f on T. Thus[3],

$$\frac{dn}{dt} = bn\left[\left(\frac{T}{\Theta}\right)^3 e^{-Q/kT} - \left(\frac{n}{n_0}\right)^2\right], \tag{3}$$

where $b = fn_0^2$ and does not depend on T.

As noted above, the total time for the establishment of the equilibrium concentration of the holes and electrons depends on their initial concentration. Near equilibrium, however, the characteristic time is fully defined and as seen from (3), equals $b^{-1}e^{Q/kT}$, which indeed determines the physical meaning of b.

For the numerical estimates given below, we assume $f \approx 3 \times 10^{-30}$ cm^{-6} sec^{-1}, which leads at $\Theta \sim 1$ eV to $b \sim 10^{14}$ sec^{-1}. The characteristic time for the electron-electron interaction at $n = n_0$ is found to be reasonable, $\sim 10^{-13} - 10^{-14}$ sec. The balance equation for the electron and hole energy will be approximately written in the form

$$3kn\frac{dT}{dt} = 3kna(\Theta - T) - Q\frac{dn}{dt}, \tag{4}$$

where a is a constant characterizing the exchange of the electron energy with the lattice, and k is Boltzmann's constant. The second term in the right side of Eq. (4) is the energy lost to ionization. Finally, it would be necessary to write the equation for the change of the

[2] The equations are similar to those describing the kinetics of gas ionization behind a shock-wave front; a detailed description of this process and references to the literature can be found in [5].

[3] We can add a term that takes into account the ionization by phonons, $g(\Theta)$; this term is important for the initiation of the process but is small compared with that written out for the region of interest to us, where $L \sim 1$.

lattice temperature:

$$C_v \frac{d\Theta}{dt} = -3kna(\Theta - T). \tag{5}$$

Estimates show that in alkali-halide salts the specific heat of the electrons is small compared with the specific heat of the lattice down to temperatures on the order of 2--3 eV, i.e., $T \sim Q/3$. Therefore, the changes of Θ in this region can be neglected. At higher temperatures, when an appreciable redistribution of the energy between the lattice and the electrons takes place, this redistribution causes the substance to become condensed inside the front of the shock wave, and simultaneously causes energy to be drawn further from the striker producing the shock wave itself. In other words, in this case to calculate the changes of $\Theta(t)$ it is necessary, besides taking (5) into account, to make use of a gas-dynamic calculation of the shock-wave front structure. In the estimates presented below we have equated Θ to the equilibrium temperature of the lattice and of the electrons throughout.

Practically independently of the concrete choice of the initial values of T(0) and n(0) (provided only they satisfy the condition $n(0) \ll n_0 \exp[-Q/2k\Theta]$; $T(0) < \Theta$), at first there is a short period in which the electron temperature changes with practically no change of their concentration. This is followed by the onset of the next period, in which the temperature ceases to change, having reached the value T_1, since the entire energy acquired by the electrons is consumed in the increase of the number of electrons in the conduction band. This temperature T_1 can be readily determined from Eqs. (3) and (4), neglecting the recombination in (3) and putting dT/dt = 0 in (4).

We obtain the equation for T_1 in the form

$$3kan(\Theta - T_1) = bQn\left(\frac{T_1}{\Theta}\right)^3 e^{-Q/kT_1} \tag{6a}$$

and accordingly

$$\frac{dn}{dt} = bn\left(\frac{T_1}{\Theta}\right)^3 e^{-Q/kT_1} = \text{const} \cdot n. \tag{6b}$$

We see therefore that so long as the temperature is constant the concentration of the electrons in the conduction band and of the holes in the valence band increase exponentially in time. This growth continues until the second term of (3) becomes comparable with the first. The temperature and the concentration of the electrons then approach the equilibrium values.

To solve the system (3) and (4) we employ in the latter case the following method. We seek the solution in the form

$$y = y_0 + (1 - y_0)\,\text{th}\,A(x - x_0), \tag{7}$$

$$z = z_0 - \frac{3}{p}(y - y_0) + \frac{3}{p}(1 - y_0)\left[x - x_0 - \frac{1}{A}\ln\text{ch}\,A(x - x_0)\right], \tag{8}$$

where

$$y = \frac{T}{\Theta}, \quad z = \ln\frac{n}{n_0}, \quad x = at, \quad p = \frac{Q}{\Theta}.$$

We equate y_0 to the quantity $(T_1 + \Theta)/2\Theta$. The values of the constants z_0, A, and x_0 are found from the condition y = 1 at $x \to \infty$, from Eqs. (4) and (3) with $y = y_0$, and from the known value z_1 at the chosen instant x_1 when $y_1 = T_1/\Theta$. Comparison of the solution obtained by this method with the exact solution obtained

with an electronic computer has shown that it is adequate for estimates.

To find the light flux radiated by the front it is necessary to know, besides the electron temperature, also the absorption coefficient α. The dependence of α on T and n is chosen analogous to that used in[3], in the form

$$\alpha = \frac{1.69 \cdot 10^{-2}}{n} \frac{n\Gamma}{\omega^2 + \Gamma^2} [\text{cm}^{-1}], \qquad (9)$$

where the refractive index is

$$n = \sqrt{1 + (\varepsilon_\infty - 1)\delta}, \quad \Gamma = 1.34 \cdot 10^{15} \left(\frac{1}{e} - \frac{1}{e}\right)\sqrt{T[\text{ev}]}[\text{sec}^{-1}],$$

δ is the relative density, ϵ_0 and ϵ_∞ are the static and high frequency dielectric constants, ω is the frequency of the light whose flux is measured. For the blue region $\omega = 6.27 \times 10^{14}$ sec^{-1}, and for the red region $\omega = 4.8 \times 10^{14}$ sec^{-1}. The light flux F in relative units is equal to

$$F = \int_0^l F_0(T)\alpha \exp\left\{-\int_0^l \alpha\, dl\right\}dl, \qquad (10)$$

where $F_0 = (e^{\tau/T} - 1)^{-1}$, $l = (D - U)t$, and U and D are the mass and wave velocities of the shock wave. For blue light $\tau = 2.593$ eV, and for red light $\tau = 1.985$ eV.

The theory considered above is valid at temperatures on the order of 1 eV and above. At temperatures ~0.5 eV and below it must be modified somewhat. The point is that, as shown in[3], at such temperatures the light emits electrons excited not from the valence band but from certain levels in the forbidden band. These levels correspond to defects generated by the shock wave propagating through the solid crystal. In the liquid state, such levels can arise in natural fashion as a result of the disordered nature of the structure.

Equations (3) and (4) go over in the case of defects to the following equations:

$$\frac{dn}{dt} = \frac{n_{\text{д}}}{2n_0} bn\left[\left(\frac{T}{\Theta}\right)^{3/2} e^{-q/kT} - \frac{2n^2}{n_0 n_{\text{d}}}\right], \qquad (3a)$$

$$\frac{3}{2} kn \frac{dT}{dt} = 3kan(\Theta - T) - q\frac{dn}{dt}. \qquad (4a)$$

In these equations, q is the defect excitation energy and n_{d} is the concentration of the defects.

COMPARISON OF THEORY WITH EXPERIMENT

A. High Temperatures

The theory considered above was used to calculate the brightness temperatures of the shock compressed ionic crystals investigated in[1]. A comparison of the calculated and experimentally-measured temperatures for KCl is shown in Fig. 1. We see that by choosing the value $a = 10^{10}$ sec^{-1} it is possible to describe quite satisfactorily the experimental data, including the difference between the temperatures measured in the blue and in the red regions of the spectrum. The same value of a describes satisfactorily also the results obtained for NaCl and Kbr. The results of the calculation for LiF are likewise in good agreement with experiment at sufficiently high temperature. In this case, owing to the large width of the energy gap (Q = 11.2 eV),

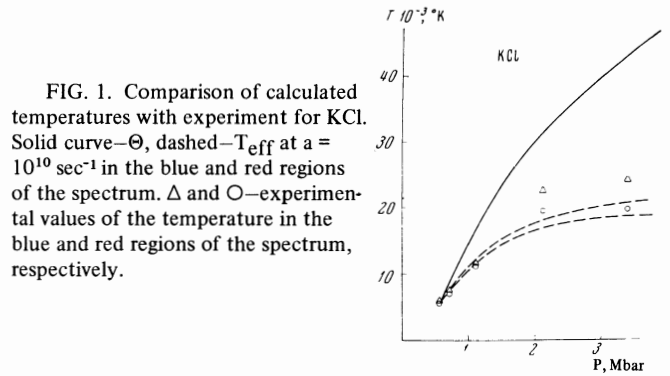FIG. 1. Comparison of calculated temperatures with experiment for KCl. Solid curve—Θ, dashed—T_{eff} at a = 10^{10} sec^{-1} in the blue and red regions of the spectrum. Δ and O—experimental values of the temperature in the blue and red regions of the spectrum, respectively.

the concentration of the electrons and the role of the screening are relatively small. This makes the brightness temperature in LiF, unlike in CsBr at the same temperature ($\Theta = 2$ eV), close to the equilibrium value. In CsBr, although calculation with a = 10^{10} sec^{-1} results in an appreciable lowering of the visible temperature (see the dashed line in Fig. 2), no satisfactory agreement with experiment is attained at pressures above 2 Mbar. Better agreement can be obtained by decreasing a to 10^9 sec^{-1} (see the line with the long dashes in Fig. 2).

It should be noted at the same time that no account was taken in the calculation of the possible narrowing of the energy gap with increasing density of the substance, leading to a lowering of the visible temperature. Nor did the calculations take into account the change of the lattice temperature during the course of establishment of the equilibrium temperature. This can play a major role in the analysis of the experimental results in the region P > 8 Mbar, where the electronic specific heat begins to exceed the specific heat of the lattice. For example, at P = 6 Mbar the equilibrium temperature equals ~5 eV, and when the contribution of the electrons is disregarded the value is ~18 eV.

As seen from (6) the change of Θ and of other parameters has relatively weak (logarithmic) influence on T_1. But when Θ is decreased, owing to the corresponding change in the wave and mass velocities of the shock wave, the rate of growth of the optical thickness is accelerated, leading to an intensification of the
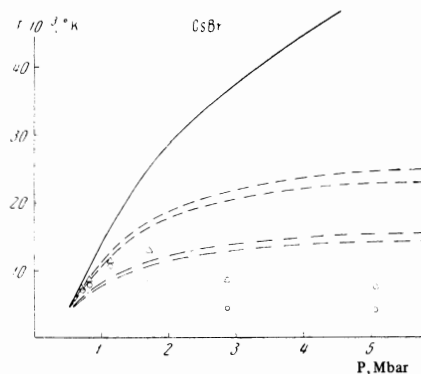

FIG. 2. Comparison of the calculated temperatures with the experimental ones for CsBr. The symbols are the same as in Fig. 1. Long dashes—T_{eff} at a = 10^9 sec^{-1}.
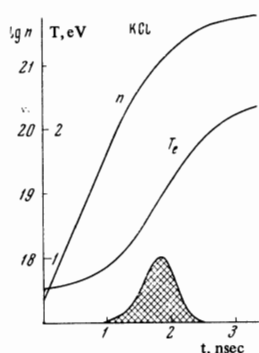
FIG. 3. Change of electron concentration n in the conduction band and of their temperature T with time in KCl at $\Theta = 2.2$ eV.

FIG. 4. Time dependence of light flux radiated by the shock-wave front. Solid curve—experiment, dashed—calculation at different values of ν_0.

screening and to a decrease of the brightness temperature.

Figure 3 shows the time dependences of the electron concentration in the conduction band n and of the temperature of the electrons T, calculated analytically (see above) for KCl at P = 1.64 Mbar and $\Theta = 2.22$ eV. The forward boundary of the shock-wave front is aligned in this figure with the ordinate axis. After $t \approx 4 \times 10^{-11}$ sec, the electron temperature reaches a value T = 0.77 eV, which it retains up to $t \approx 3 \times 10^{-10}$ sec. By that time the electron concentration in the conduction band reaches n = 1.4×10^{18} cm^{-3}. The subsequent rapid increase of n causes the absorption coefficient α to increase, so that only a rather thin layer, lagging the leading front boundary by $(1.5-2.0) \times 10^{-9}$ sec, produces the radiation.

The relative contribution of the different layers of the substance inside the shock-wave front to the radiated light flux is shown in Fig. 3 by the cross-hatched area. The emission of the deeper layers, where the electron temperature reaches its equilibrium value sufficiently rapidly (with $\Delta t \sim 10^{-9}$ sec), is screened by the forward layers with $T \sim \Theta$. The radiation registered in this case corresponds to a temperature T = 1.36 eV.

Thus, as seen from Fig. 3, the effective (brightness) temperature is somewhat higher than T_1. By way of illustration we present one example. In CsBr at P = 2.4 Mbar we have $T_{eq} = \Theta = 2.84$ eV, but $T_1 = 0.72$ eV and $T_{eff} = 1.77$ eV.

The considered mechanism of the phenomenon explains also the cause of the small reflectivity of the front of the shock wave registered in[1], in spite of the high equilibrium electron concentration, which reaches values on the order of 10^{22} cm^{-3}, which are comparable with the concentration of the free electrons in metals. The change of the electron concentration, from $n \sim 10^{18}$ cm^{-3}, when it has no influence on the reflection coefficient, to $n \sim 10^{22}$ cm^{-3}, occurs within a time on the order of 10^{-9} sec, or in a layer of thickness $\Delta \sim 5 \times 10^{-4}$ cm. At the same time, for reflection of the incident light it is necessary to have $\Delta \ll 10^{-5}$ cm.

B. Low Temperatures

In the temperature region $\Theta \lesssim 0.5$ eV, the thermal excitation of the electrons from the valence band is insignificant. Therefore, to explain the emissivity of the shock-wave front, a hypothesis was advanced in[3] that the electrons are thermally ionized from donor
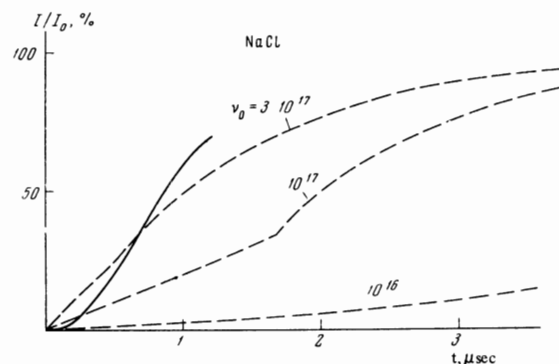
levels generated upon shock compression of the crystal. The calculation of the kinetics is carried out here on the basis of Eqs. (3a) and (4a). The calculations show that screening in the indicated temperature region is small in practice, owing to the low electron concentration. This means that the temperatures measured in[2] actually correspond to the equilibrium temperatures. However, to explain the growth of the light flux emitted by the shock wave as a function of the time, which was experimentally observed in[4] (see Fig. 4), for example, for NaCl at P = 0.45 Mbar and $\Theta = 0.23$ eV, it is necessary that the initial concentration of the electrons in the conduction band be[4] $\nu_0 \approx 3 \times 10^{17}$ cm^{-3} at a = 10^{10} sec^{-1}. This is seen from Fig. 4, where the experimental data, represented by the solid curve, are compared with the calculated curves at ν_0 equal to 3×10^{17}, 10^{17}, and 10^{16} cm^{-3}. The concentration of the defects and their energy level were taken from[3]: $n_d = 1.6 \times 10^{19}$ cm^{-3}, q = 2.4 eV. The value of ν_0 does not influence the estimates made above at higher temperatures.

It is interesting that the notions originally developed to explain the lag of the observed temperature from the equilibrium value also explain successfully the phenomena occurring at low temperature. In this region, the registered light fluxes turned out to be much larger than those expected from calculation[4]. This phenomenon is sometimes related to electroluminescence, but this does not explain the mechanism in any way. The equilibrium spectrum of this radiation ($T_{blue} \approx T_{red}$) is likewise unusual for luminescence[4]. Our explanation is based on the notion that defects are generated by the shock wave and that a number of electrons in excess of equilibrium are "injected" into the conduction band.

When the shock-wave amplitude in NaCl is decreased to P = 0.27 Mbar, at $\Theta = 0.117$ eV, the initial "injection" of electrons into the conduction band ν_0 remains most likely the same as before. We assume further that energy exchange between the electrons and the lattice is of very low probability. The latter is

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4)We shall not concern ourselves here with the mechanism whereby these electrons appear in the conduction band. We assume that they are "injected" there as a result of plastic deformation of the lattice by the shock wave (see below).

equivalent to assuming $a = 0$ in (3a). Then Eq. (3a) can be readily integrated; when this result is taken into account, Eq. (4a) becomes

$$\frac{3}{bq}\frac{n_0}{n_d}\frac{dT}{dt} = \frac{2\nu_0^2}{n_0 n_d}e^{3h(T_0-T)/q} - \left(\frac{T}{\Theta}\right)^{3/2}e^{-q/kT}. \tag{11}$$

Equation (11) describes the kinetics of the establishment of thermal equilibrium between the electrons. The same equation can yield the stationary temperature of the electrons T_1. In the concrete case of NaCl we have $T_1 = 0.215$ eV $= 2500°$K, whereas in this case $\Theta = 1360°$K. This is just the brightness temperature registered under these conditions in NaCl[4].

A similar calculation for LiF ($q = 3.7$ eV, $n_d = 10^{19}$, $\nu_0 = 3.5 \times 10^{17}$) leads to a brightness temperature $T_{br} \approx 4000°$K at $\Theta = 0.185$ eV, i.e., also confirms the possibility of the clearly pronounced nonequilibrium radiation (relative to Θ) observed in[4] although, unlike in NaCl, not all the experimental points can be described as satisfactorily for this radiation. An important factor in the proposed explanation is the assumption that the initial "injection" of the electrons and holes has a nonequilibrium character and is not determined by the lattice temperature. A quantitative description of the nonequilibrium "injection" is a still unsolved problem.

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