

PHOSPHORESCENCE AND CONDUCTION CURRENT RELAXATION IN ZnSe CRYSTALS

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INTRODUCTION

In scintillation crystals, at X-ray or gamma quanta registration, a noticeable time delay of the pulse is observed. This is due to the thermal delocalization of charge carriers from traps. The study of phosphorescence and relaxation of the conduction current can give information on these processes. It is convenient to use ZnSe single crystals as a model crystallophosphor to build a general kinetic theory of luminescence and conductivity. These crystals have a sufficiently intense stationary luminescence, phosphorescence, thermoluminescence and stationary conduction current, conduction current relaxation, thermally stimulated conductivity under UV and X-ray excitation, which allows measuring luminescence and conductivity simultaneously.

1. EXPERIMENTAL METHODS

The ZnSe single crystals were grown from the pre-cleaned charge and not doped during their growth. As a result, we obtained crystals with minimum concentration of point defects and maximum resistivity ($\geq 10^{12} \Omega \cdot \text{cm}$ - $10^{14} \Omega \cdot \text{cm}$). For the study purposes, the samples of $18 \times 9 \times 2 \text{ mm}^3$ were cut from two different crystal boules and polished. To study the conductivity, the indium electric contacts in the form of two parallel bands ($1 \times 5 \text{ mm}^2$, i.e. $L = 5 \text{ mm}$) were sprayed onto the single crystals. Copper electrodes were soldered to the contacts distanced to $d = 5 \text{ mm}$. The indium selected as a contact provided the ohmicity of the contact. Studies of current-voltage characteristics have confirmed that such contacts are ohmic. A stabilized voltage from 0 to 1000 V was applied to one electrode, while another contact was grounded via a nanoamperemeter. The nanoammeter allowed to measure the current from 1 pA to 10 pA with an accuracy of 10%, from 10 pA to 100 pA with an accuracy of 3 %, and from 100 pA to 1 mA with an accuracy of <1%. For all values of the conductivity current, the condition was fulfilled that the input impedance of the nanoamperemeter is several orders of magnitude less than the electrical resistance of the ZnSe sample. The nanoamperemeter is a part of the specially developed measuring block which allows to choose the voltage change mode: stepped or monotonic with possibility of smooth change of voltage with various speed.

2. EXPERIMENTAL RESULTS

2.1 Luminescence spectra

Characteristic X-ray luminescence (XRL) spectra for single-crystal ZnSe samples in the spectral range from 400 to 1200 nm at different temperatures (8 - 420 K) consist of two known [1-7] wide luminescence bands with maxima at 630 nm (1.92 eV) and 970 nm (1.28 eV). The spectra of different high-impedance samples differ only in the ratio of the intensities of these two main luminescence bands. Boundary luminescence and luminescence of donor-acceptor pairs in high-impedance ZnSe samples were not recorded.

The band at 630 nm, according to [2, 3], is due to the complex center which includes the zinc vacancy, and the band with a maximum at 970 nm is due to the complex center with the vacancy of selenium [4, 5]. Both luminescence bands are due to the recombination mechanism of luminescence, as they are observed in phosphorescence and TSL [8]. The spectral maxima of these bands [6,7] do not change much with temperature, which allows them to be recorded at a fixed wavelength at different temperatures.

Photoluminescence (PL) spectra upon excitation of these ZnSe samples by UV quanta with an energy greater than the band gap almost coincide with the XRL spectra [8,9]. There is a noticeable difference only in the spectral position of the maximum of the band at 630 nm.

2.3. Phosphorescence and current relaxation at different excitation intensities

The luminescence spectra of high-resistance ZnSe crystals during phosphorescence (Ph) and TSL coincide with the spectra of stationary XRL and PL [8]. This greatly simplifies the simultaneous registration of the glow on the two bands (630 and 970 nm) and the conduction current. Simultaneous registration of luminescence and conductivity current allows comparing them and drawing adequate conclusions. Classical kinetic theories of PL and current relaxation (CR) state that the attenuation curves should be the same after the same radiation doses. Verification of this fact showed (Fig. 1) that this is not the case. The same dose of X-irradiation can be obtained by decreasing the intensity of X-excitation (I_X) and increasing the time of excitation (t_X) by the same number of times. Fig. 1 shows current relaxation (curves 1 and 2) ($U_0 = 15 \text{ V}$) and phosphorescence in the band 630 nm (curves 3 and 4) of ZnSe sample at a temperature of 85 K after X-ray excitation at the same dose (7.62 mJ/cm^2), but at different X-ray intensities $I_{X1} \cdot t_{X1} = (I_{X1}/5) \cdot (5t_{X1})$.

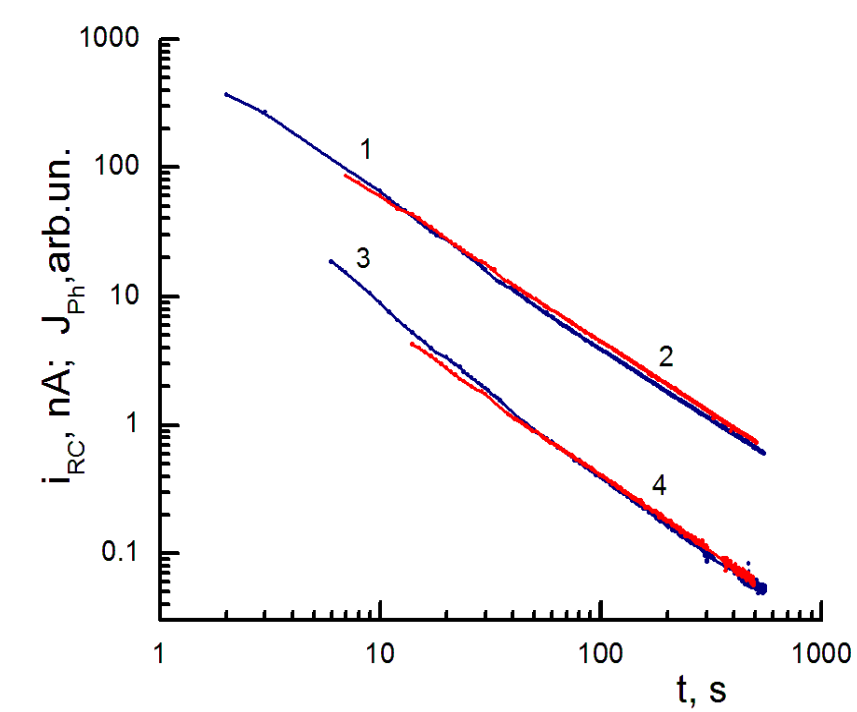


Fig.1 Current relaxation (1, 2) ($U_0 = 15 \text{ V}$) and phosphorescence in the band 630 nm (3, 4) of the ZnSe sample at a temperature of 85 K after X-ray excitation with the same dose (7.62 mJ/cm^2) at different intensities of X-ray irradiation $I_{X1} \cdot t_{X1} = (I_{X1}/5) \cdot (5t_{X1})$

After phosphorescence recording TSC and TSL in the bands 630 and 970 nm were recorded. The corresponding curves of TSC and TSL practically coincide with each other (Fig. 2). Slightly larger accumulated light sum ($\sim 10\%$) at lower intensity of X-excitation is probably due to the fact that a slightly larger part of the generated free charge carriers goes to localization compared to recombination.

It should be noted that the ratio of the intensities of the peaks of TSL and TSC are different in different samples, which indicates a different concentration of different traps in different

ZnSe crystals. Most of the charge carriers are thermally delocalized from the traps when heated to a temperature of 250 K, which indicates the dominance of the concentration of shallow traps in the investigated material. The most high-temperature maximum (very weak) is observed at $T_m = 292 \text{ K}$ on the TSC curves.

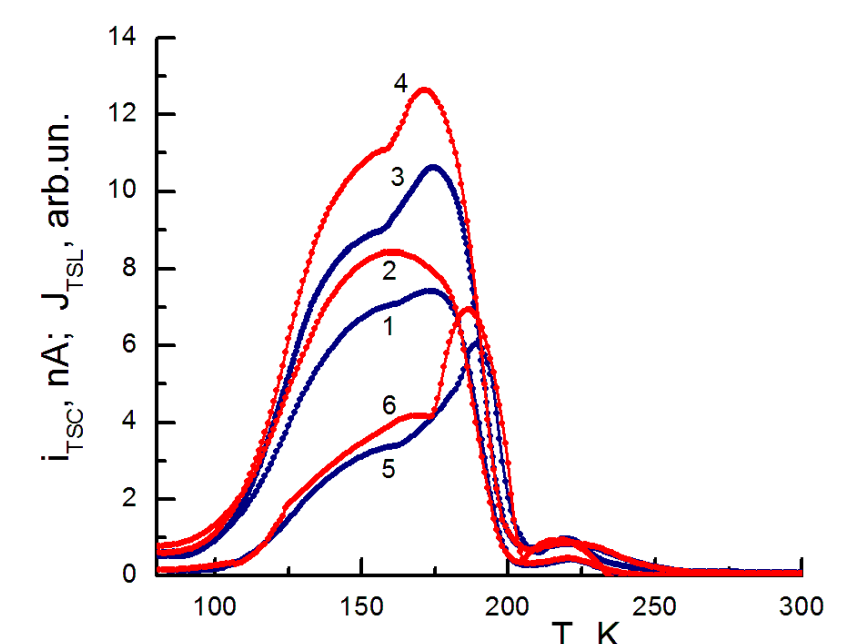


Fig.2 TSC (1,2) ($U_0 = 15 \text{ V}$) and TSL in the band 630 nm (3,4) and in the band 970 nm (5,6) of ZnSe sample after X-excitation at a temperature of 85 K with the same dose (7.62 mJ/cm^2), at intensity I_{X1} and time t_{X1} (1,2,3) and at intensity I_{X2} and time t_{X2} (4,5,6)

Analysis of the temperature position of the peaks of TSL and TSC in ten different samples of single-crystal ZnSe shows that there are peaks from one set, and their intensities differ significantly in different samples. That is, for ZnSe single crystals there is a certain set of traps and different samples differ only in the ratio of their concentrations. Moreover, this set of traps corresponds to the data [10] and is subject to the formula of a harmonic oscillator.

3. Theoretical dependences for Ph intensity and CR

Classical kinetic theories of luminescence and conductivity are not suitable for the theoretical determination of kinetics of Ph intensity attenuation and CR, because they use the model of crystallophosphors with one type of traps and one center of luminescence. However, in real crystals there are always a significant number of traps (several peaks on TSL and TSC curves). A multicenter model reflects the situation in crystals more adequately and contains four types of electron traps (small, phosphorescent, deep) and one glow center with an electronic recombination mechanism at the excitation temperature. For such division of traps it is possible to use three criteria: average life time of a charge carrier on a trap (τ_i); a maximal level of trap filling during prolonged excitation (n_i/v_i), i.e. when a quasi-equilibrium state is reached; location of a trap level relative to the Fermi electronic level in the restricted area. However, these criteria give the same result. At the excitation temperature T_0 , traps for which $\tau_{i-1} < 1 \text{ c}$, $n_{i-1}/v_{i-1} \ll 1$ and the level of which is above the Fermi level (at least by several kT) we will consider as shallow traps. The phosphorescent trap is a trap for which $\tau_i \sim 1-100 \text{ c}$, $n_i/v_i \sim 1/2$ and its level is near the Fermi level. It is this trap that determines the main in-

tensity of phosphorescence. Traps for which $\tau_{i+1} \gg 100 \text{ c}$, $1/2 < n_{i+1}/v_{i+1} < 1$ and their levels are below the Fermi level in the forbidden zone we will consider as deep ones. Next, all types of shallow traps are combined into one effective shallow trap with an index "s". Similarly, all deep traps are also combined into one effective deep trap with an index "d". Phosphorescent trap is denoted by an index "ph". This model of crystallophosphorus will be called a multicenter model. For such a model of a crystal, we can write a system of kinetic equations and obtain approximate solutions in analytical form. Theoretical dependences for the phosphorescence intensity and the magnitude of the relaxation current for such a model of crystallophosphorus were obtained in [11]. It was taken into account that all acts of delocalization of electrons from traps and their subsequent localization or recombination are independent processes. The obtained theoretical dependence was in the form of the sum of three exponents. Each exponent is due to the delocalization of charge carriers from shallow, phosphorescent or deep traps. The time constants of the exponents are determined not only by the lifetime of the carriers on the trap, but also depend on the ratio of the concentrations of this trap to the concentration of the deeper trap.

If we take into account the change in the concentration of recharged glow centers where recombination of charge carriers delocalized from traps takes place, then an additional multiplier appears in each exponent. In many crystals, the concentrations of shallow traps (v_s) are higher than the concentrations of phosphorescent (v_{ph}) and deep traps (v_{d1}), which is observed in TSL and TSC after different excitation temperatures. Also it is necessary to add superdeep traps with concentration (v_{d2}) in calculations. Delocalization of electrons from superdeep traps during phosphorescence can be neglected, but free electrons can be localized on them, affecting Ph attenuation and CR curves.

The expressions for magnitude of current relaxation and phosphorescence intensity:

$$i_{RC}(t) = i_{0s} \sum_{k=1}^{k_{\text{max}}} \frac{m_k^k \exp(-m_k)}{k!} \exp(-t/(k+1)\tau_s) + \frac{i_{0ph}}{(1/\tau_{ph}^* - 1/(m_s+1)\tau_s)} \left(\frac{\exp(-t/\tau_{ph}^*) - \exp(-t/(m_s+1)\tau_s)}{1 + r_{ph}m_{ph} [1 - \exp(-t/\tau_{ph}^*)]} \right) + \frac{i_{0d1}}{(1/\tau_{d1}^* - 1/\tau_{ph}^*)} \left(\frac{\exp(-t/\tau_{d1}^*) - \exp(-t/\tau_{ph}^*)}{1 + r_{d1}m_{d1} [1 - \exp(-t/\tau_{d1}^*)]} \right) \quad (1)$$

$$J_{ph} = J_{0s} \sum_{k=1}^{k_{\text{max}}} \frac{m_k^k \exp(-m_k)}{k!} \exp(-t/(k+1)\tau_s) + \frac{J_{0ph}}{(1/\tau_{ph}^* - 1/(m_s+1)\tau_s)} \frac{\exp(-t/\tau_{ph}^*) - \exp(-t/(m_s+1)\tau_s)}{1 + r_{ph}m_{ph} [1 - \exp(-t/\tau_{ph}^*)]} + \frac{J_{0d1}}{(1/\tau_{d1}^* - 1/\tau_{ph}^*)} \frac{\exp(-t/\tau_{d1}^*) - \exp(-t/\tau_{ph}^*)}{1 + r_{d1}m_{d1} [1 - \exp(-t/\tau_{d1}^*)]} \quad (2)$$

It is these theoretical dependences (1) and (2) that should be compared to experimental data. They take into account the re-storage on those traps from which the delocalization of electrons occurs (which led to a more complex function than the exponent for a trap emptying) and intermediate localizations on more shallow traps as well.

4. Longtime current relaxation and phosphorescence

The significant concentration of traps in ZnSe crystals allows registering Ph and CR during a long time (up to 2 hours) at low temperatures (8 and 85 K) after photo- and X-excitation. The corresponding attenuation curves are shown in Fig. 3 and Fig. 4. The absence of accumulation of light on deep traps at room temperature is also confirmed by the absence of noticeable phosphorescence at this temperature. And at low temperatures (8 and 85 K) there is a noticeable Ph, which indicates the presence of traps of different depths.

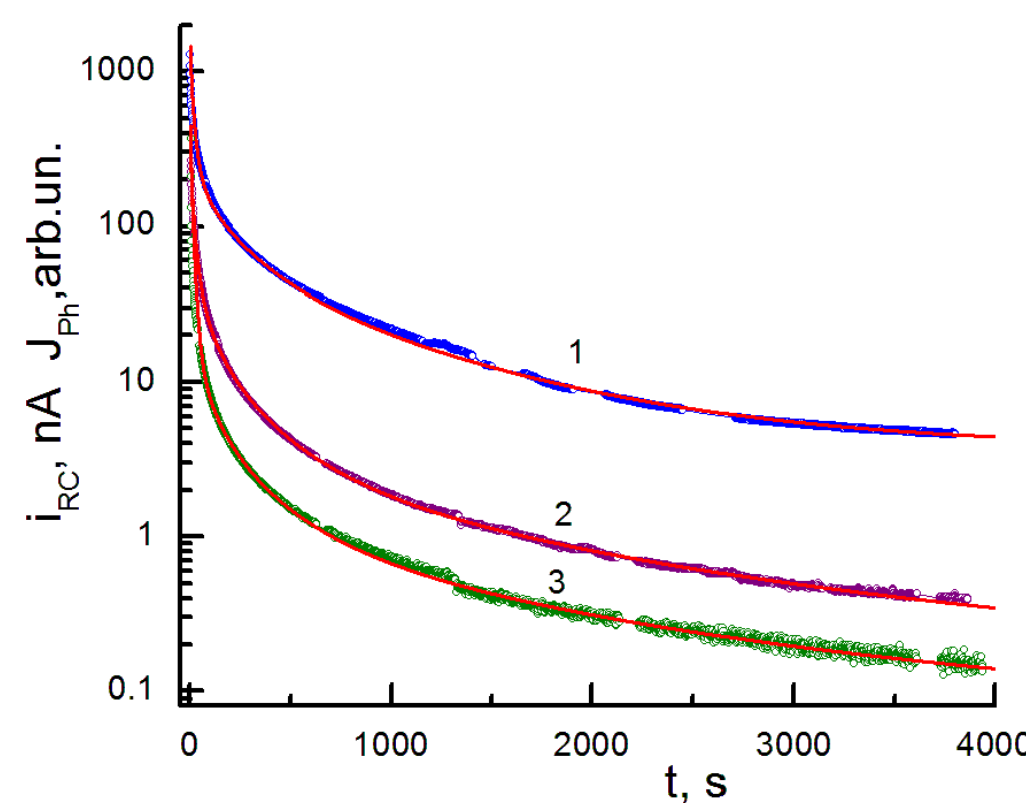


Fig.3 Longtime current relaxation (1) ($U_0 = 15 \text{ V}$) and phosphorescence in the band 630 nm (2) and in the band 970 nm (3) of the ZnSe sample at a temperature of 8 K after X-ray excitation (points - experimental values, lines - theoretical dependences (1) and (2)).

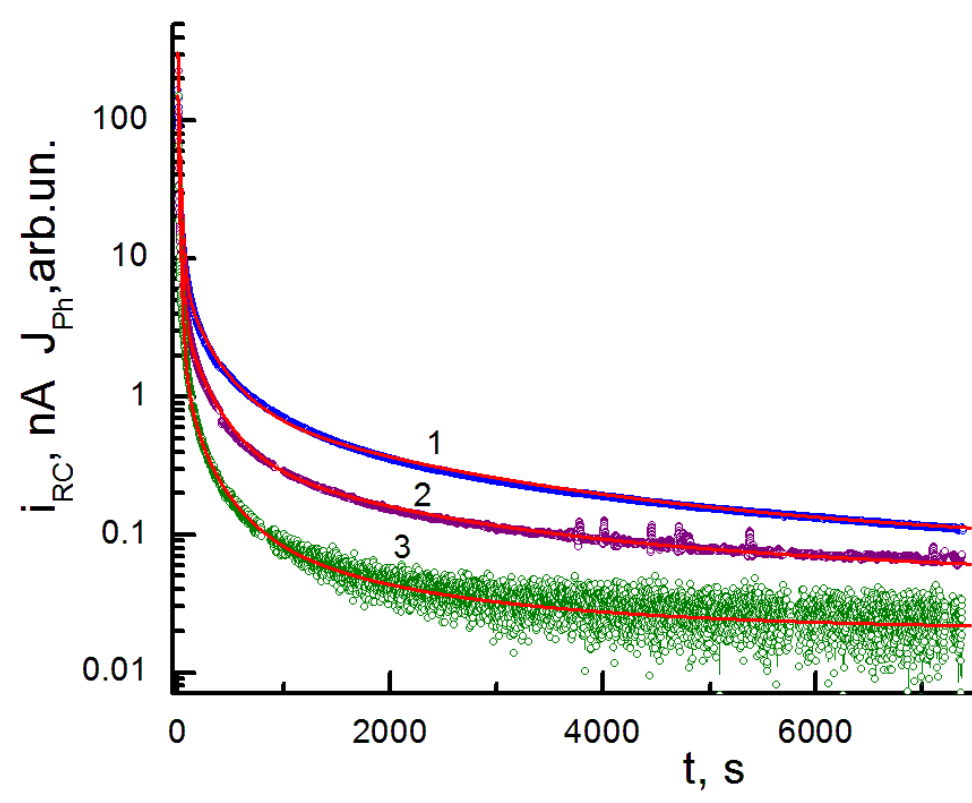


Fig. 4 Longtime current relaxation (1) ($U_0 = 15 \text{ V}$) and phosphorescence in the band 630 nm (2) and in the band 970 nm (3) of the ZnSe sample at a temperature of 85 K after X-ray excitation (points - experimental values, lines - theoretical dependences (1) and (2)).

CONCLUSIONS

Investigation of long-term phosphorescence and conduction current relaxation of specially undoped high-impedance ZnSe crystals of high optical quality at different temperatures have shown that it is due to the delocalization of charge carriers from almost all traps. Moreover, in the process of relaxation there is an intermediate localization of carriers on more shallow traps. Theoretical dependences for the phosphorescence intensity and the magnitude of the conduction current are obtained in analytical form. They take into account the intermediate acts of localization of charge carriers on more shallow traps.

An experimental fact that the phosphorescence and relaxation curves of the conduction current at the same irradiation dose, but at different excitation intensities and, accordingly, different excitation times, intersect is explained. This experimental fact contradicts the classical kinetic theory of luminescence. It is determined that at the excitation temperature at least three types of traps (shallow, phosphorescent and deep) take part in phosphorescence and conduction current relaxation. Therefore, it is necessary to use a multicenter model of crystallophosphorus. Moreover, the level of filling of various traps depends not only on the total radiation dose, but also on the intensity of excitation.

References

- K. Katrunov, V. Ryzhikov, V. Gavriluk, S. Naydenov, O. Lysetska, V. Litichevskiy, Optimum design calculations for detectors based on ZnSe(TeO) scintillators, Nuclear Instruments and Methods in Physics Research (A), 712, (1) (2013) 126-129.
- V.M. Koshin, A.Ya. Duffan, V.D. Ryzhikov, L.P. Gal'chinskii, M.G. Starzhinskiiy, Thermodynamics of isovalent tellurium substitution for selenium in ZnSe semiconductors // J. Functional materials. - 2001.- v. 8, N4 - p. 708-713.
- L.V. Atroschenko, L.P. Gal'chinskii, S.N. Galkin, V.D. Ryzhikov, V.I. Silin, Structure defects and phase transition in telluriumdoped ZnSe crystals // J. Cryst. Grows. - 1999.- v.197.- p. 475-479.
- N.K. Morozova, I.A. Karetnikov, V.V. Blinov, E.M. Gavrishechuk, Semiconductors. - 2001.- № 1 - p. 24-32.
- N.K. Morozova, I.A. Karetnikov, V.V. Blinov, E.M. Gavrishechuk, Semiconductors. - 2001.- № 35 (5) - p. 512-515.
- M. Alizadeh, V.Ya. Degoda, B.V. Kozhushko, N.Y. Pavlova, Luminescence of Dipole-
- centers in ZnSe crystals, Functional Materials. - 2017.- v.24, No.2 - p. 206-211.
- M. Alizadeh, V.Ya. Degoda, The spectra of x-ray and photoluminescence of high-resistance crystals of ZnSe, Ukr. J. Phys. - 2018.- V.63, N.6 - C. 557-562.
- M. Alizadeh, V.Ya. Degoda, The spectra of X-ray and photoluminescence of high-resistance crystals of ZnSe, Ukr. J. Phys. 63, (6) (2018) 557-562.
- V.Ya. Degoda, M. Alizadeh, Ya.P. Kogut, N.Yu. Pavlova, S.V. Sulima, The influence of UV excitation intensity on photoconductivity and photoluminescence in ZnSe monocrystals, Journal of Luminescence, V. 205, 2019, Pages 540-547.
- V. Degoda, A. Gumenjuk, N. Pavlova, A. Sofienko and S. Sulima, Oscillatory Regularity of Charge Carrier Trap Energy Spectra in ZnSe Single Crystals // Acta Physico Polonica A. - 2016. - Vol. 129, No. 3. - pp. 304-309.
- Brody M.S., Degoda V.Y., Alizadeh M., Podust G.P., Pavlova, N.Y., Kozhushko, B.V. Deep traps concentrations in ZnSe single crystals. Materials Science and Engineering B: Solid-State Materials for Advanced Technology, 2020, 258, 114570