

In Fig. 2 we compare the results of the glow curves analysis, both for ZnS_z and for ZnS_w after pressure treatment at $1,200 \text{ Kpcm}^{-2}$. As may be seen, the TL data confirm once again the aforesaid differences between the zincblende modification obtained by thermal process and that obtained by

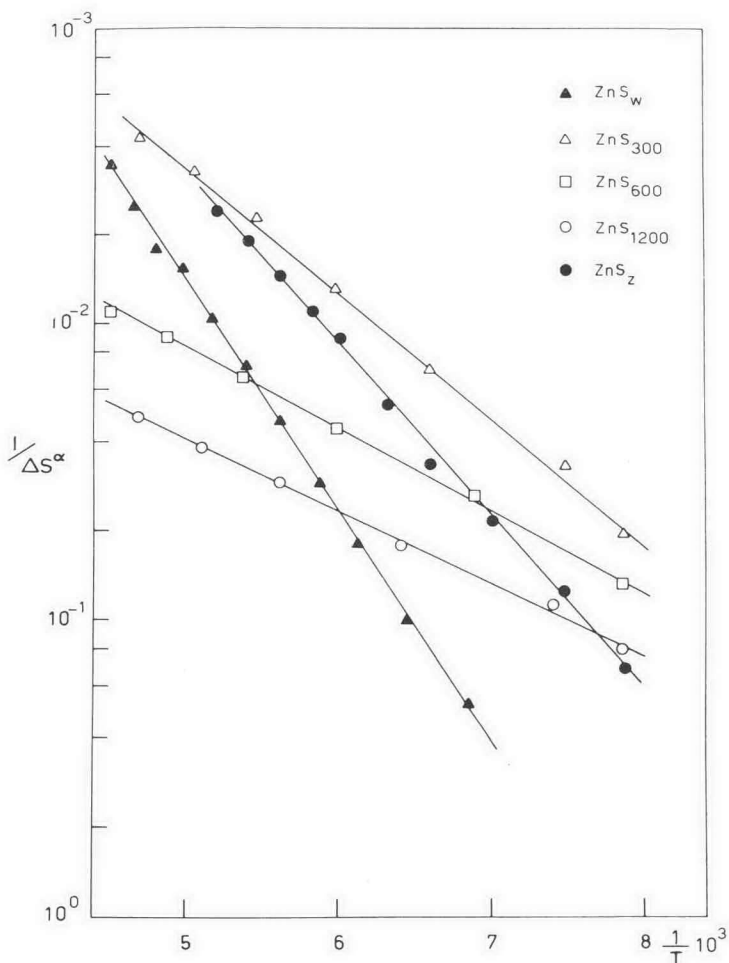


Fig. 3 - Plot of $\ln(I/\Delta S^\alpha)$ versus $1/T$ for all the examined samples.

pressure treatment. In Fig. 3 we show directly the rectified curves for all samples studied. The results are collected in Table 1.

From this, it can be seen that while the kinetic order is 1.35 for both the ZnS modifications thermally obtained, it goes to 1.00 for all the pressed samples.

TABLE 1 - Kinetic order (α) and activation energy (E) for different ZnS samples.

	ZnS _w	ZnS ₃₀₀	ZnS ₆₀₀	ZnS ₁₂₀₀	ZnS _z
α	1.35	1.00	1.00	1.00	1.35
E(eV)	0.15 ± 0.01	0.08 ± 0.01	0.06 ± 0.01	0.05 ± 0.01	0.12 ± 0.01

On the other hand, as regards activation energy of the trapping centers, it is true that the values found for the samples after pressure treatment are inferior to those of wurtzite and zincblende thermic modifications, but they are decreasing functions of the pressure. Moreover, for both kinds of samples the activation energy shows a direct proportionality with the width of the forbidden gap [2].

4. Discussion.

From Table 1 it can be seen that the pressed samples all present a monomolecular type kinetic. This may be attributed to the fact that the density m of the recombination centers is much higher than the density n of the electrons taking part in the TL process, or vice-versa.

In order to explain this fact, let us remember that the pressed samples are characterized by the existence of electron trapping centers, due to the broken tetrahedral bonds [2]. When a free electron interacts with the electron localized in a broken bond, it may form a singlet state of energy lower than that of the conduction band. In this way each singlet state subtracts two electrons to the sulphur vacancy trapping levels, that are responsible for the thermoluminescence [8]. Consequently, the density n of the electrons that contribute to the TL process will be reduced, which is also in agreement with the lesser luminescence emission observed in all the pressed samples. If the reduction of n is such that $n \ll m$, then the electron-hole recombination will depend only on the density m of the recombination centers. This is just one possible explanation of the monomolecular kinetic found in the TL process of the pressed samples.

On the other hand, the fact that the activation energy in all the pressed samples is much lower than in those not pressed suggests the hypothesis that the pressure treatment can modify the trapping level localization into the band gap.

Finally, we feel that the lesser intensity of the thermoluminescence in the pressed samples may be attributed, besides to the already mentioned reduction