

EXCITON SPECTRA OF ZnS CRYSTALS WITH STACKING FAULTS

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ZnS is a typical representative of an extensive group of crystals having two polymorphic modifications - cubic (sphalerite) and hexagonal (wurtzite) [1]. The structure of sphalerite (wurtzite) can be represented as two mutual interpenetrating closest cubic (hexagonal) packings of sulfur and zinc ions. When the crystal grows in the closest packing plane, defects can be produced, i.e., a regular arrangement of the closest-packing layers. Thus, in cubic ZnS there are produced layers which are arranged in accordance with hexagonal packing (and vice-versa). If we characterize the crystal by means of the probability α that the closest-packing layer contains defects and we put $\alpha = 0$ for sphalerite, then $0 < \alpha < 1$ for sphalerite with stacking faults and wurtzite can be regarded as a structure with $\alpha = 1$.

The exciton spectra of cubic and hexagonal ZnS are known [2,3]. We investigated the exciton spectra of ZnS crystals with an appreciable concentration of stacking faults.

We obtained the reflection spectra of crystals of four types. 1. Sphalerite obtained by hydrothermal synthesis. The crystals are quite perfect in structure ($\alpha = 0$). 2. Sphalerite grown from the melt under pressure. The large number of stacking faults makes the crystals anisotropic* ($\alpha = 0.10^{**}$). 3. Sphalerite grown by the same method but with addition of 0.01% of aluminum; the introduction of the impurities stimulates the formation of defects and increases α to 0.25. 4. Wurtzite, grown from the gas phase, perfect crystals ($\alpha = 1$).

The spectra were obtained at $T = 4.2^\circ\text{K}$. The reflection lines (reflection angle 25°) had the shape of a normal dispersion curve. The resonant frequency was assumed to be midway between the maximum and minimum of the dispersion curve. Figure 1 shows schematically the spectra of the investigated crystals. For comparison, Fig. 2 shows the energy band structures sphalerite and wurtzite at the point $k = 0$.*** The trigonal complement of the crystal field splits the band Γ_8 of sphalerite into two bands, Γ_9 and Γ_7 (and also mixes the bands Γ_8 and Γ_6). It can also be noted that the width of the forbidden band and the spin-orbit splitting are larger in wurtzite than in sphalerite.

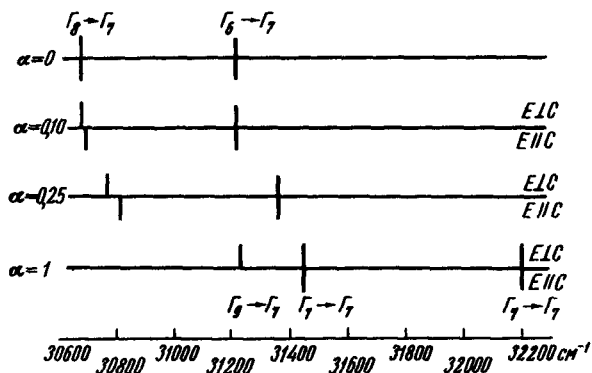


Fig. 1

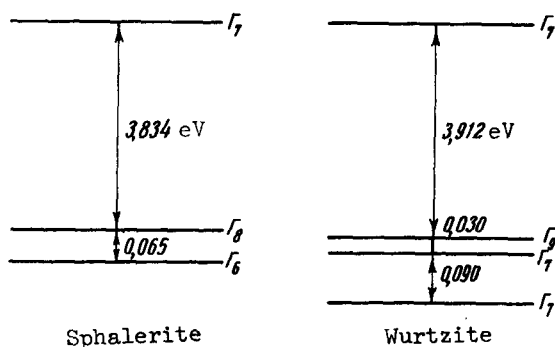


Fig. 2

It is seen from Fig. 2 that the occurrence of stacking faults in sphalerite crystals leads to a splitting and shifting of the exciton lines; both effects increase with increasing stacking-fault concentration****. These changes in the spectrum are obviously the consequence of the splitting and shifting of the energy bands of the sphalerite under the influence of the average field V of the stacking faults, which are irregularly distributed over the crystal (along a threefold axis)*****.

Thus, from the point of view of the large-radius exciton*****, a crystal with stacking faults is a new medium with parameters that depend on the stacking-fault concentration.

It is of interest to trace the $V(\alpha)$ dependence. One might think that at small values of α , when the distances between the stacking faults becomes commensurate with R , the exciton ceases to sense the stacking faults on the average, and is only scattered by them.

Indeed, an analysis of the experimental data shows that the shift and splitting of the exciton lines of sphalerite depends nonlinearly on α , and is particularly disproportionately small when $\alpha = 0.10$ (on the order of 1% of the splitting and shifting of the lines on going from sphalerite to wurtzite)*****.

To the contrary, for ZnS polytypes it was found (in the region $0.1 < \alpha < 0.5$) that the intrinsic absorption edge splits (in two polarizations) and shifts linearly as a function of α [4]. Apparently the different character of the dependence of α in these two cases is due to the fact that electrons with $k \sim 2\pi/\lambda$ are generated in interband transitions ($\lambda \approx 3000$ Å - wavelength corresponding to the intrinsic absorption edge), and when the wave function of the exciton is constructed, use is made of the \bar{k} -space region with $(k) \sim \pi/R$.

Since $\lambda \gg R$, the averaging over the stacking faults extends in the former case to much lower values of α than in the latter, and the deviations from the linearity at $\alpha \sim 0.1$ will be negligibly small for the interband transitions.

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* In sphalerite there are four closest-packing planes, {111}, in each of which a stacking fault can be produced in principle. However, the crystal grows along a definite {111} plane, and the stacking faults are produced precisely in this plane; this singles out one of the four threefold axes [111] (which coincides with the [0001] axis of wurtzite in the region of the stacking fault), thus making the crystal anisotropic.

** The value of α was determined from the birefringence δn under the assumption that δn is proportional to the number of layers formed in accordance with the hexagonal closest packing, i.e., that $\delta n = \alpha \delta n_0$ (δn_0 - birefringence of wurtzite). The foregoing relation was verified with ZnS polytypes (structures with regular alternation of cubic and hexagonal packing), for which δn and α can be determined independently [4].

*** In view of the fact that the binding energy of the exciton in ZnS is small (~ 0.05 eV), the exciton spectrum reflects directly the structure of the energy bands of the crystal

at the point $\bar{k} = 0$.

**** The changes in the narrow-line spectra of the ZnS crystals with stacking faults were noted in [5].

***** The possibility of introducing an average potential in the analysis of the band scheme of ZnS crystals with stacking faults was first pointed out by Birman [6].

***** The Bohr radius of the exciton in ZnS is $R = 30 \text{ \AA}$ [3].

***** When $\alpha = 0.10$, the average distance $l = d/\alpha$ between the stacking faults ($d = 3.1 \text{ \AA}$ - distance between two closest-packing layers) is equal to 31 \AA , i.e., it practically coincides with R .

MEASUREMENT OF TEMPERATURES OF SHOCK-COMPRESSED CCl_4 AND OF A $\text{CCl}_4\text{-C}_6\text{H}_6$ SOLUTION

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Information on the equation of state of substances (particularly organic ones) at high pressures can be obtained by studying states attained under shock compression. The shock adiabats of certain organic liquids were determined in [1,2] and in a number of other papers; on the basis of a statistical reduction of these data, the following general formula was proposed for organic substances [3]:

$$D = 1.2C_0 + 1.7U,$$

where D is the shock-wave propagation speed, U the speed of the substance behind the wave front, and C_0 the speed of sound in the substance in the initial state. Calculation using this formula makes it possible to predict the dynamic compressibilities with an accuracy sufficient for the solution of most gasdynamic problems. At the same time, there are practically no published data on the shock-compression temperatures of organic liquids.

We report here the results of measurements of the brightness temperature of shock-compressed carbon tetrachloride (CCl_4) and a 63/37 carbon tetrachloride and benzene (C_6H_6)

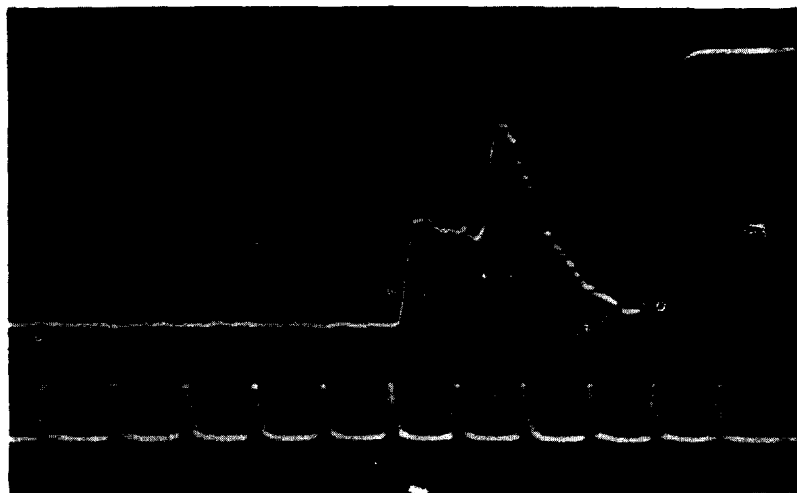


Fig. 1. Shock-front brightness oscillogram