

## Layered semiconductor GeS as a birefringent stratified medium

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Transmission and reflection spectra of GeS single crystals of different thicknesses have been measured in a wide spectral range. The interference spectra have two periods in unpolarized light, one of which is the usual Fabry-Pérot type while the other is due to birefringence. It is also shown that the reflection coefficient in the transparent region depends on the crystal thickness and reaches the value of about 0.75 for thick crystals ( $\sim 800 \mu\text{m}$ ). The results obtained have been analyzed by using the  $4 \times 4$  matrix method for multilayer optical systems. It is shown that GeS can be considered as a natural birefringent stratified medium.

GeS is a layered semiconductor with orthorhombic crystalline structure with space symmetry group  $D_{2h}^{16}$ . The unit cell parameters in the plane of the layers are  $a = 4.30 \text{ \AA}$ ,  $b = 3.65 \text{ \AA}$ . In the perpendicular direction, GeS has a lattice parameter  $c = 10.45 \text{ \AA}$ .<sup>1</sup> GeS exhibits a pronounced anisotropy in optical properties.<sup>2</sup>

Due to the crystal symmetry that it possesses, GeS is an optically biaxial crystal. According to the ellipsometric measurements of Ref. 3, the values  $n_a = 3.33$ ,  $n_b = 3.49$ ,  $n_c = 2.9$  were obtained. In Ref. 4, 3.176 for  $n_a$  and 3.358 for  $n_b$  have been reported. Analyzing the existing data for refractive indices of GeS,<sup>3-6</sup> one observes that the relation  $n_c < n_a < n_b$  holds in all cases.

The layered crystalline structure of GeS as well as the other layered crystals make it very easy to investigate the interference spectra when light is incident perpendicular to the layer planes. This method has been used to determine the refractive indices of many layered semiconductors including GeS crystals.

In the present paper, the results of the investigations of the interference in the transmission and the reflection spectra of GeS single crystals at room temperature are presented. These spectra have some characteristics (as reported in Ref. 7) that cannot be explained on the basis of the known optical properties of GeS. According to our results, GeS can be considered as a birefringent stratified medium, which makes this crystal an important candidate to be used in many optoelectronic devices. To our knowledge, this is the first demonstration of optical effects about the evidence of a birefringent stratified medium in a single crystal.

Detailed investigations of the transmission spectra of GeS samples of different thicknesses (Fig. 1) recorded in a wide spectral range within the transmission region show that the interference spectra of GeS have some interesting features. Curves 1-4 in Fig. 1 represent four different types of interference spectra obtained with unpolarized light for samples of different thicknesses at room temperature. The experiments with polarized incident light have shown that the type of spectra did not depend on the polarization of incident light.

(1) Samples of 10-30  $\mu\text{m}$  thickness: The spectrum recorded in a wide spectral range (curve 1 in Fig. 1, obtained for the sample with  $d = 22 \mu\text{m}$ , gives only a small

part of the spectrum) shows that it is doubly periodic. The second much larger period shows up as a considerable reduction in the interference amplitude with the adjacent singularities separated by a wavelength interval obeying the well-known rule  $\Delta\lambda \sim \lambda^2$ . The refractive index determined from the simple condition for a maximum or a minimum of the Fabry-Pérot interference is in agreement with the available data ( $n \simeq 3.2$ ), if the "normal" period of interference  $\Delta\lambda$  is used in the relation  $n \simeq \lambda^2/2d\Delta\lambda$ . If the new interference period is formally used, the value obtained for  $n_s$  (subscript  $s$  denotes that it is the smaller value for  $n$ ) is close to 0.4 throughout the whole investigated spectral range.

The two-period nature of the interference spectra appears to be, not only in the amplitude modulation of the normal interference pattern, but also in a simultaneous frequency modulation. This frequency modulation represented by periodic variation in the intervals between the adjacent maxima (and minima) is seen clearly in the case of a thicker sample, which is discussed below.

(2) Sample with  $d = 60 \mu\text{m}$  (curve 2 of Fig. 1): In addition to the compression of the interference pattern

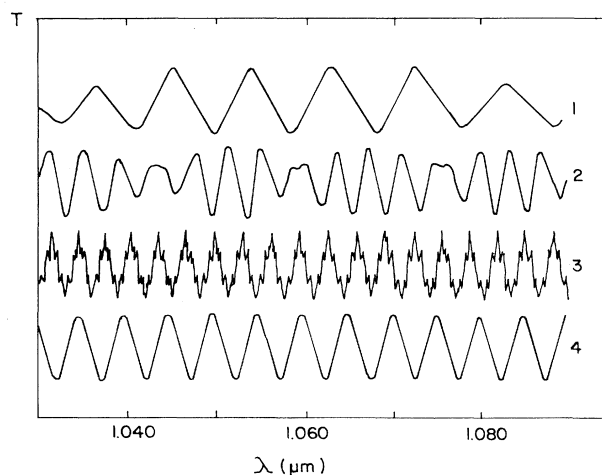


FIG. 1. The transmission spectra of GeS sample crystals of different thicknesses: (1) 22  $\mu\text{m}$ , (2) 60  $\mu\text{m}$ , (3) 300  $\mu\text{m}$ , and (4) 770  $\mu\text{m}$ .

due to the relatively larger thickness of this sample, the two-period nature of the spectrum can be seen clearly as a frequency modulation of the interference. As in the case of the sample of thickness  $22\text{ }\mu\text{m}$ , the value of  $n_s$  remains the same (at 0.4), but there is a considerable change in  $n$  inferred from normal interference, that is from the intervals between the nearest extremes. It is evident from curve 2 that the values of  $n$  are about 1.8.

(3) Sample with  $d = 300\text{ }\mu\text{m}$ : The interference spectrum of this sample is also doubly periodic, but in contrast to thinner samples, the depth of the amplitude modulation corresponding to  $n_s$  is much larger than that of the normal refractive index  $n$ . For this sample, the values of  $n_s$  and  $n$  are 0.4 and 1.8, respectively. In the case of poor spectral resolution or at shorter wavelengths where adjacent extremes become closer to each other, the interference pattern becomes singly periodic with "small refractive index" 0.4.

(4) Sample with  $d = 770\text{ }\mu\text{m}$ : It should be noted that this sample was taken from a technologically different batch. It is evident from Fig. 1, curve 4, that the interference spectrum is singly periodic with  $n_s = 0.14$ . The spectrum of the thinner sample, which was obtained from the same batch, appeared to be doubly periodic with  $n_s = 0.14$  and  $n = 3.2$ , i.e., the value  $n_s = 0.14$  is typical for the samples obtained from this batch.

To obtain information about the refractive indices of the investigated samples, measurements of the reflection coefficients were carried out with spectral resolution worse than in the case of the interference spectra. In this case, there was no interference pattern in the reflection spectra.

Figure 2 shows the reflection coefficient of the sample with  $d = 770\text{ }\mu\text{m}$ , characterized by  $n_s = 0.14$  and  $n = 3.2$ . Spectral behavior typical of many layered semiconductors is seen: The reflection coefficient rises steeply when the photon energy becomes lower than the band gap. In all the previously reported investigations, this rise in the transparent region is attributed to the multiple reflection of light from the surface opposite to that

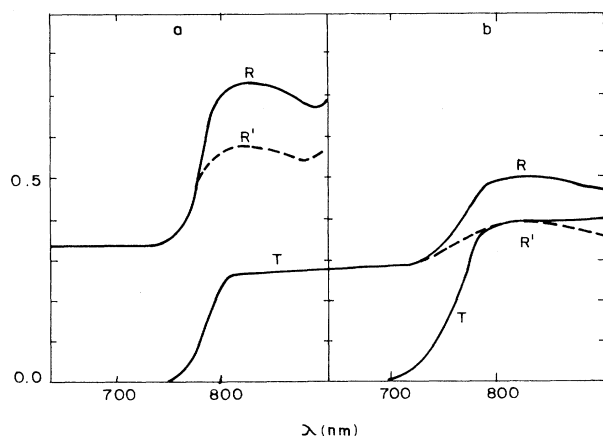


FIG. 2. Reflection ( $R_H$ ,  $R$ ) and transmission ( $T$ ) spectra of GeS crystals of thicknesses (a)  $770\text{ }\mu\text{m}$  and (b)  $70\text{ }\mu\text{m}$ .  $R$  is the reflection coefficient found after subtraction of the effects of the multiple reflection from the back side of the crystal.

which is illuminated.

As can be seen from Fig. 2, in the transparent region the value of the transmission coefficient is almost equal to one minus the reflection coefficient, i.e., there is practically no absorption. Thus, it can be easily shown that the high value of the reflection coefficient in the  $h\nu < E_g$  region in GeS cannot be explained only by the multiple reflections from the back side of the crystal. A simple calculation yields that the value for the reflection coefficient after subtracting the multiple reflections appeared to be  $R = 0.6$  (dashed curve in Fig. 2) in the transparent region, which is in contrast with the normal value  $n = 3.2$  if one uses the simple Fresnel formula.

Figure 3 gives the reflection spectra of the thinner specimen ( $d = 70\text{ }\mu\text{m}$ ) obtained from the same batch ( $n_s = 0.14$ ). It is seen that the value of  $R$  in the transparent region decreases considerably while the transmission coefficient increases. If we subtract now the multiple reflection effects from the back side of the crystal, the value of the reflection coefficient becomes close to the normal one.

Thus, in GeS crystals, there is a considerable thickness dependence in the reflection coefficient, i.e., the reflection coefficient is higher in the thicker crystals. It is now necessary to note that these experimental results can be achieved only in high resistivity single crystals, which exhibit very small absorption in the transparent region.

The presence of a second much larger period in the

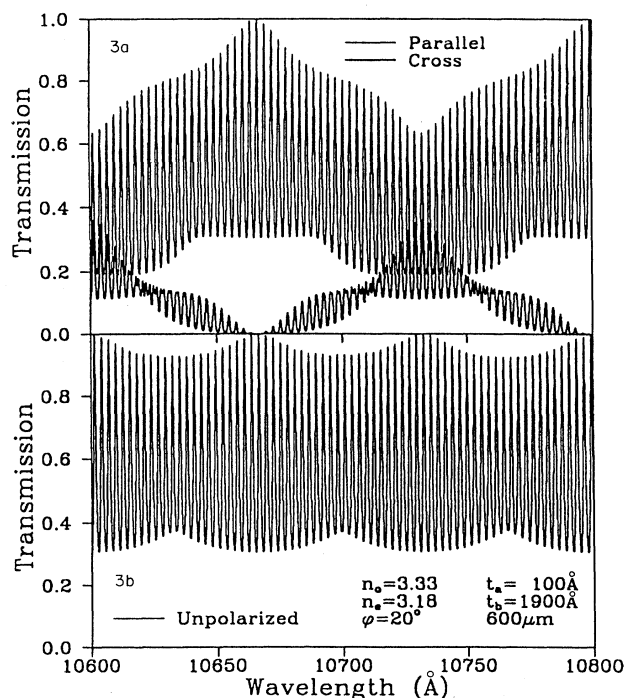


FIG. 3. Transmission spectra of the Solc-filter model of a birefringent stratified media for cross and parallel polarizer and analyzer (a), and for unpolarized light (b). Total thickness is  $600\text{ }\mu\text{m}$ . The values of used parameters are shown:  $n_o$ ,  $n_s$ : refractive indices,  $t_a$ ,  $t_b$ : thickness of the layers (in Å),  $\varphi$ : angle between optical axes of successive layers.

interference spectra shows that in addition to the usual Fabry-Pérot mechanism GeS exhibits another interference of a different origin. Because of the beats in the interference spectra of the thinner samples, one can conclude that there are two main rays with close values of refractive indices, characterizing GeS crystals, which give usual Fabry-Pérot interference and also can interfere with each other. This effect can be a consequence of birefringence, which seems quite realistic for GeS.

Then, one has to explain the following facts: (a) the possibility of interference of rays polarized along mutually perpendicular directions (note that our experiments were carried out without analyzer), (b) the dependence of interference pattern on crystal thickness, and (c) the different values of higher period characterizing  $n_s$  for the crystals obtained from different batches.

We think that all of the above peculiarities of the interference spectra can be explained by taking into account the high value of reflection coefficient in the transparent region of the thick sample ( $t = 770 \mu\text{m}$ ) and its smaller value in the thinner one ( $\sim 70 \mu\text{m}$ ) (Fig. 2). These results confirm that multiple reflections within the crystal must occur, i.e., GeS can be regarded as a stratified medium with alternate layers having different optical constants.

At the present time it is rather difficult to show the nature of this stratification. We believe that it may be connected with the layer structure of GeS or more precisely with its particular defect structure. As is well known, the most important defects existing in layer crystals are stacking faults of layers leading to the mixture of different polytypes of crystals in the specimen. According to recent structural investigations,<sup>8</sup> the existence of extended planar defects are also characteristics of GeS and GeSe. Thus, together with its orthorhombic crystalline structure, it seems rather reasonable to consider GeS as a birefringent stratified medium.

The simplest model of a birefringent stratified media considered in the literature is the folded Solc-filter model<sup>9</sup> in which each layer in the stratified medium is uniaxial with optical axis lying in the plane of layer. Each plate is rotated with respect to its neighbors by some angle  $\phi$  in order to produce a periodically stratified medium.

It is well known<sup>8</sup> that the  $4 \times 4$  matrix method describes the optical properties of a multilayer structure like the Solc-filter model taking into account both the multiple reflection effects between the adjacent layers and the birefringence. We have used this simple model to give at least a qualitative explanation of our interference spectra.

In Figs. 3 and 4, a small part of the transmission spectra of our model in the spectral range close to the transparent region of GeS is presented. The values of the parameters used in the calculations are given in each figure. The value of  $n_o - n_e$  was chosen to be close to  $n_b - n_a$  in GeS to take into account the conditions of the experiments. The following main results have been obtained using the Solc-filter model of a birefringent stratified medium for GeS.

As can be seen from Fig. 3(b) the interference spectrum for unpolarized light are doubly periodic and look like experimentally observed ones with thin ( $d < 30 \mu\text{m}$ )

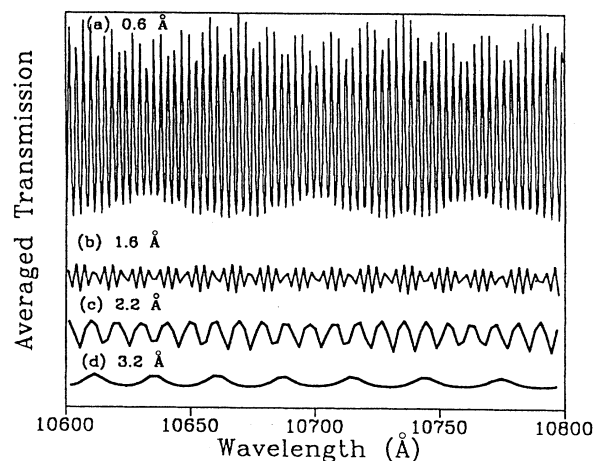


FIG. 4. The transmission profiles after spectral averaging for the samples having the same parameters as in Fig. 3, for the averaging intervals 0.6 Å (a), 1.6 Å (b), 2.2 Å (c), and 3.2 Å (d).

samples. The smaller period of interference gives the value of refractive index close to  $n_a$  and  $n_b$  and thus corresponds to Fabry-Pérot interference of the whole stack of the layers. The second higher period, which we characterized by  $n_s$ , gives values close to  $n_b - n_a$  in GeS.

It is more favorable (from the point of view of the symmetrical interference pattern) to assume neighboring layers with large difference of thicknesses. The last fact becomes more important when a small number of layers, for example,  $N < 50$  is used. Thus, it is better also to use the high number of layers (more than 100) with different thicknesses to obtain interference patterns close to the experimental ones.

According to the calculations, the type of interference spectra, or rather the type of modulation, remains unchanged as the crystal thickness changes, which seems to contradict the experimental results. [See Fig. 3(b) for the sample with a thickness of  $600 \mu\text{m}$ ]. It can be shown that the evolution of the interference spectra while increasing the crystal thickness may be obtained by making spectral averaging of theoretically calculated spectra. It seems quite reasonable that spectral averaging effects become more and more important when crystal thickness increases. In fact, in thick samples ( $d \geq 100 - 200 \mu\text{m}$ ) crystal imperfections (thickness nonuniformity, internal imperfections, etc.) may play quite an important role.

Figure 4 demonstrates the results of spectral averaging using the well-known relation

$$T(\lambda) = \frac{1}{\lambda_1 - \lambda_2} \int_{\lambda_1}^{\lambda_2} t(\lambda) d\lambda,$$

where  $t(\lambda)$  is the theoretically calculated spectrum,  $T(\lambda)$  is the averaged one, and  $\lambda_1 - \lambda_2 = \delta\lambda$  is the averaging interval.

As it becomes clear from the figures, many details of the experimentally observed spectra can be obtained from the theoretical calculations by the spectral averaging procedure. At the smallest averaging interval, the

interference spectrum is close to the experimentally observed one for the thin sample. By increasing the averaging interval, the experimental interference spectra registered for the thicker specimens can be obtained. As can be seen from Fig. 4(a), for the smallest averaging interval, two periods in the interference patterns correspond to  $n \sim 3.2$  and  $n_s \sim n_b - n_a$ . Thus, the first period corresponds to Fabry-Pérot interference and the second one to birefringence.

In thicker samples, interference spectra obtained after spectral averaging may have two-period and one-period nature. The values of  $n_s$  obtained in both of these spectra are higher than  $n_b - n_a$  and approach the values that we have observed experimentally and those in Ref. 4, namely, 0.4, 0.8, and 1.2. The normal refractive index obtained from two-period spectrum in this case appeared to be smaller than 3.4 (for example, 1.8).

Now, note that the value of  $n_s \sim 0.14$ , which is close to the birefringence  $n_b - n_a$  in GeS, is registered only for one type of investigated crystals. We think that it is because of the high quality of the crystals, i.e., containing a smaller number of imperfections as mentioned

above. That is why the sample with  $d = 70 \mu\text{m}$  having this quality still demonstrates the interference pattern characteristic of "thin" samples, whereas the less perfect one of  $60 \mu\text{m}$  thickness appeared to be "thicker." Moreover, the samples investigated in Ref. 4 with  $d = 30 \mu\text{m}$  having one-period interference spectra with  $n_s \simeq 0.7$  are "thicker" than the former two.

In conclusion, we believe that the Solc-filter model of a birefringent stratified medium for GeS is the simplest one and other models of stratification may also be used. As was mentioned above, it is difficult to discuss various models of real crystalline structure of GeS without detailed structural investigations. What we can say at the present time is that GeS (and probably its analogs GeSe, SnS, SnSe) can be considered as natural models of a birefringent stratified medium.

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