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Autor: Fischer, Gaston
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Speculation on the Band Structure of the Layer Compounds GaS and GaSe

by **Gaston Fischer***)
Division of Pure Physics, National Research Council, Ottawa, Canada.

(20. X. 62)

Abstract. The two compounds GaS and GaSe are characterized by structures built up by the stacking of distinctive layers and it is therefore tempting to consider each layer as a two-dimensional conductor. Each single layer has trigonal symmetry, with the trigonal c-axis being perpendicular to the layer. The reduced Brillouin zone of these two-dimensional crystals is therefore a hexagon. The number of molecular units, e.g. GaSe, per unit cell is two, so that there are 18 valence electrons. The compounds are semiconductors and thus the first nine zones are full, with the energy gap lying between the 9th and 10th zones. Construction of the free electron sphere, here a circle, suggests that the valence band has either a single or a two-fold maximum at the zone centre. The conduction band, on the contrary, appears to have extended minima on the zone sides and a single minimum at the zone corner. These theoretical considerations are compared with the experimental data and a more detailed band structure is then proposed.

1. Introduction

A great deal of experimental data has recently been collected about the three compounds, GaTe, GaSe and GaS. In particular the structures of all three substances are now known unequivocally (BASINSKI *et al* 1961, BRYDEN 1963). Optical, galvanomagnetic, and photoconductive data at various temperatures are also available (specific references will be given at appropriate places). It is therefore tempting to make use of this material in order to deduce a plausible band structure.

The determination of the band structure of a given solid is generally approached from theoretical as well as experimental sides, whereby theory provides an overall band picture and experiments then give more precise information on certain details. For the gallium compounds under investigation no theoretical band calculation is presently available. Our purpose is to derive a band picture by making use of two very simplifying assumptions. We shall then check whether this speculative band picture is consistent with available experimentel data.

2. First Simplifying Assumption

The 'nearly-free-one-electron' approach having proved very successful when applied to metals, we shall follow the geometrical methods that have been used by

*) Now at Laboratories RCA, Zurich, Switzerland.

GOLD (1958) and HARRISON (1959) in the derivation of the Fermi surfaces of lead and aluminium respectively. The validity of this approach has recently been the object of extensive theoretical investigations (e.g. EHRENREICH and COHEN 1959) and will not be discussed here. Our purpose is to describe briefly and apply the methods which evolved from these recent studies. What has been shown is that over most parts of wave-vector space (or $\boldsymbol{k}$-space) the relation between energy E and wave-vector $\boldsymbol{k}$ is nearly identical to that holding for free electrons:

$$E(\boldsymbol{k}) = \hbar^2 k^2/2\, m_0 \,. \tag{1}$$

In this relation $2\pi\hbar = h =$ Planck's constant, $k = |\boldsymbol{k}|$ and $m_0 =$ free electron mass. Major deviations occur only in the vicinity of Brillouin zone boundaries, being generally such that constant energy surfaces intercept zone boundaries perpendicularly. To obtain the shape of the Fermi surface in the various Brillouin zones a sphere is drawn, the energy of which is equal to the Fermi energy E_F. Small changes are made to the sphere to ensure perpendicular interception with all zone boundaries. The different zones are then reduced into the first one, yielding various portions of Fermi surface in the different zones. This method has been followed by GOLD (1958) to obtain an overall picture of the Fermi surface of lead. GOLD (1958, 1960) then refined this first approximation with the help of experimental data that he had obtained mainly from de Haas-van Alphen experiments. HARRISON (1959) found an ingenious method which does away with the problem, sometimes difficult, of the reduction of Brillouin zones. The first zone is drawn as a repeating unit in $\boldsymbol{k}$-space. A sphere corresponding to the Fermi energy E_F is drawn around each zone centre. HARRISON has shown that points which are in one sphere correspond to states which are occupied in the first zone only. Points which are in two spheres simultaneously represent occupied states of the first and second zones. Points wich are in n spheres correspond to states occupied simultaneously in the first n zones. The surface which encloses all the points that belong to the n^{th} zone is the portion of Fermi surface in that zone. In general each portion of Fermi surface so derived reveals some 'kinks' or lines along which the surface slope is discontinuous. Smoothing out these 'kinks' corresponds, in the present method, to the corrections introduced previously to guarantee perpendicular intercepts between Fermi surface and zone boundaries.

3. Second Simplifying Assumption

The second simplifying assumption is related to a particular structural property of the compounds under investigation which all crystallize as layer structures. The atomic arrangement within a single layer is the same for GaSe and GaS, and is illustrated in Figure 1. The two compounds differ, however, in the way their layers are stacked. Each single layer is itself composed of four close-packed sub-layers in the order Se Ga Ga Se (or S Ga Ga S). Figure 1 suggests that the chemical bonds within the layers are between Ga^{-1} and Se^{+1} (or S^{+1}) ions, whereby Ga^{-1} obtains a tetrahedral sp^3 coordination and Se^{+1} (or S^{+1}) a trigonal pyramidal p^3 coordination with a saturated s^2 subshell. The bonds between the layers are essentially of the van der

Waals type, with the possibility of a very small ionic contribution. The layer separation of 3.18 Å is quite large and the shortest Se-Se distance from one layer to another is 3.84 Å, whereas the Ga-Ga and Ga-Se bond lengths within one layer are 2.39 and 2.37 Å respectively. For GaS the four corresponding lengths are very similar, being about 3.09, 3.75, 2.46 and 2.43 Å. From the foregoing considerations it would appear that each layer is a self-contained unit which is bound only very loosely to other such units. Since there is practically no overlap of the electronic wave functions from different layers we may ask whether most electronic properties of these two compounds might not be better explained with a two-dimensional rather than the usual three-dimensional band model. We believe that the almost complete absence of wave-function overlap between adjacent layers implies that electric conduction in a direction perpendicular to the layers should not be described with the standard concept of mobility. Instead, conduction in this direction, parallel to the c-axis, probably takes place by random hopping processes whereby electrons jump from one layer to another. The random mechanism may be tunnelling through the potential barrier existing between adjacent layers. We shall therefore attempt to derive the band structures of GaSe and GaS on the assumption that they reduce to only two dimensions of $\boldsymbol{k}$-space.

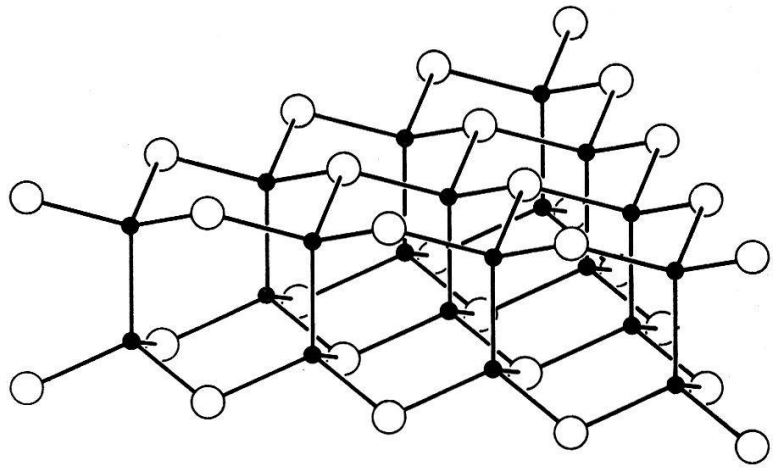

Figure 1

Structure of one of the four-fold layers of GaS and GaSe; • Ga atoms, ○ S or Se atoms.

The crystal structure of GaTe (BRYDEN 1963) is much more complex than that of the other two compounds. The very large three-dimensional monoclinic unit cell contains 12 molecular units as against two for the two-dimensional cells of GaSe and GaS. This means that there are in all 108 valence electrons, and a band structure derivation by the method outlined in Section 2 is probably meaningless. In addition, the separation between layers is much smaller in GaTe; it is therefore less likely that a two-dimensional approach is permitted. Consequently, we expect the band structure of this compound to be very complex. This conclusion is supported by the complexity of the optical absorption spectrum (BREBNER and FISCHER 1962).

4. Derivation of the Band Structure

The first step in any band calculation is to construct the Brillouin zone. Since the isolated layer shown in Figure 1 has trigonal symmetry we have a two-dimensional rhombic Bravais net with base. Our primitive cell (BARRON and FISCHER 1959) is a rhombus with an acute angle of 60°. This primitive cell is identical with the one pertaining to a hexagonal network. The first Brillouin zone, hence, is a regular hexagon which we have drawn in Figure 2 as a repeating unit in $\boldsymbol{k}$-space. Each cell contains two atoms of Ga and two of Se (or S), yielding a total of 18 valence electrons.

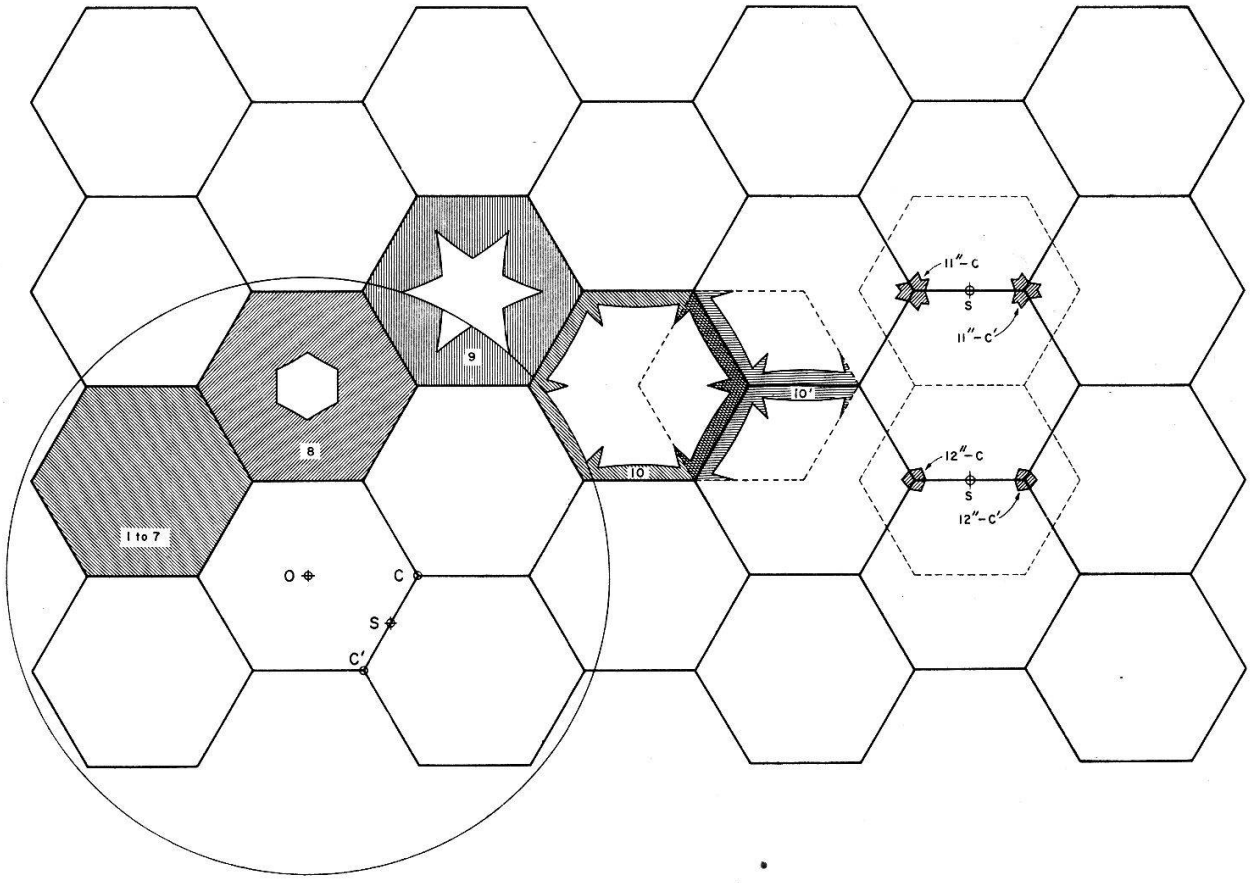

Figure 2

First Brillouin zone, drawn as a repeating unit of wave-vector space, of the two-dimensional structure shown in Figure 1. This diagram serves to the derivation of the band structures of GaS and GaSe by a method described in the text.

The Fermi sphere in three dimensions reduces here to a circle which contains 18 electronic states per primitive unit cell. In other words, the surface area enclosed by the Fermi circle must be equal to the total area of nine hexagons, since each zone contains 2 electronic states for each primitive cell. In Figure 2 we have drawn one such circle around a zone centre 0. If a circle is drawn around each zone centre and all points of $\boldsymbol{k}$-space are identified according to the number of circles to which they belong simultaneously, we arrive at the distribution depicted in Figure 2. Zones 1 to 7 are

completely filled, zones 8 and 9 are filled for the main part but have a pocket of holes at the zone centre. Zone 10 contains electrons only in the shaded areas along the zone boundaries, and zones 11 and 12 have very small pockets of electrons at the zone corners. If this were the actual distribution of electrons we would be dealing with a metal. Since, however, GaSe is a semiconductor we have to postulate that, except for thermally activated holes, all zones from 1 to 9 are fully occupied. All higher zones, on the other hand, are empty. What Figure 2 then suggests is that zones 8 and 9 correspond to valence bands which have a maximum of energy at the zone centre 0. Zones 10, 11 and 12, on the contrary, correspond to conduction bands which all have minima of energy at points like S, C, or C' of the zone edges. Zone 10 has been redrawn as zone 10′ after translating the zone boundaries; a corner point, C or C', then becomes the zone centre. Another translation has been effected for zones 11 and 12 which become zones 11″ and 12″. The sole purpose of these translations is one of convenience, as the electron pockets of zones 11 and 12 would otherwise be split up into six small pieces scattered around at the corners of a zone centred in 0. It must be remembered, however, that the new centre S of these translated zones is not equivalent with the true origin 0 of the Brillouin zones for which $\boldsymbol{k} = 0$. It should also be noted that all zones have hexagonal symmetry. The apparent reduction to trigonal symmetry of zone 10′, for example, stems from the translation and the existence of two sets of corner point, C and C', which differ by a 60° rotation. Anything holding for C also holds for C' in the appropriate orientation.

We are now in a position to give a sketch of the band structure of GaSe and GaS. In Figure 3 we plot the energy E versus the magnitude k of the wave vector along the three directions, OC, OS and CSC'. For convenience we call V_1 and V_2 the valence bands corresponding to zones 8 and 9; whereas C_3, C_4 and C_5 are the conduction bands corresponding respectively to zones 10, 11 and 12. At any given point of $\boldsymbol{k}$-space V_2 is always above V_1 but their maximum at 0 need not be very different. It is even possible that V_1 and V_2 are degenerate at the origin 0. Zone 10 appears to have constant energy contours that run almost parallel to the zone boundaries CSC', and perhaps minima in both C and S. In directions away from the zone boundaries, however, the energy increases rapidly. The $E(\boldsymbol{k})$ diagram of Figure 3 accordingly shows C_3 to remain almost level along CSC' and to increase rapidly from C and S towards 0. Bands C_4 and C_5 appear to have minima at C which are energetically very close together and increase very quickly as one moves from C. Again these two bands may be degenerate at their minimum.

We shall in the following section discuss various implications of the above band model in some detail, but we can already single out two of its most important properties. The small curvature in the viciniyt of the minima of band C_3 leads to a heavy effective mass and consequently a low mobility. We would therefore expect intrinsic GaSe and GaS to be p-type, a conclusion borne out by the Hall effect measurements on GaSe shown in Figure 4. Since the maximum of valence band V_2 and the minimum of conduction band C_3 occur at different points of the Brillouin zone we would expect the fundamental edge of the optical absorption spectra of GaSe and GaS to correspond to indirect transitions. This conclusion is also supported by experimental data, although the spectra of Figures 5 and 6 show some additional complexity that we shall discuss later.

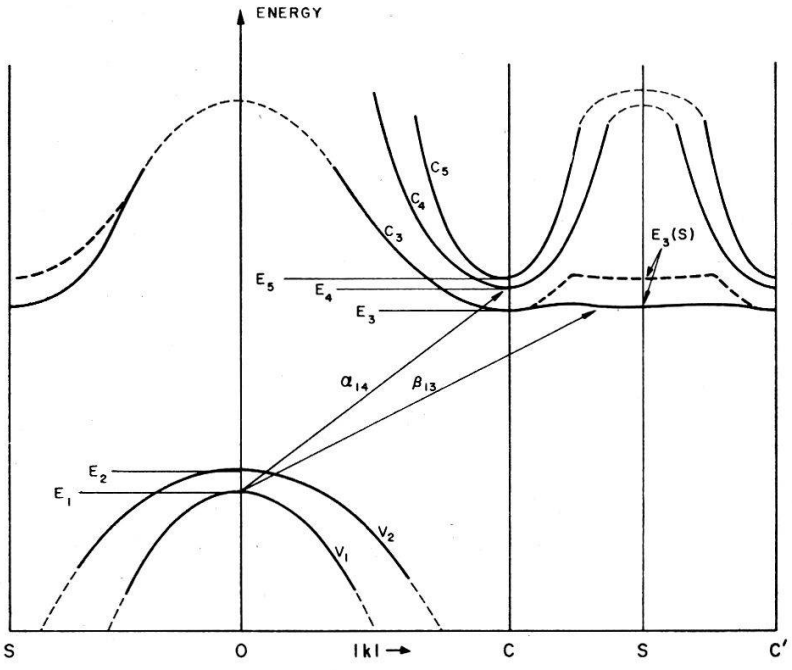

Figure 3

Schematic band structure of GaS and GaSe.

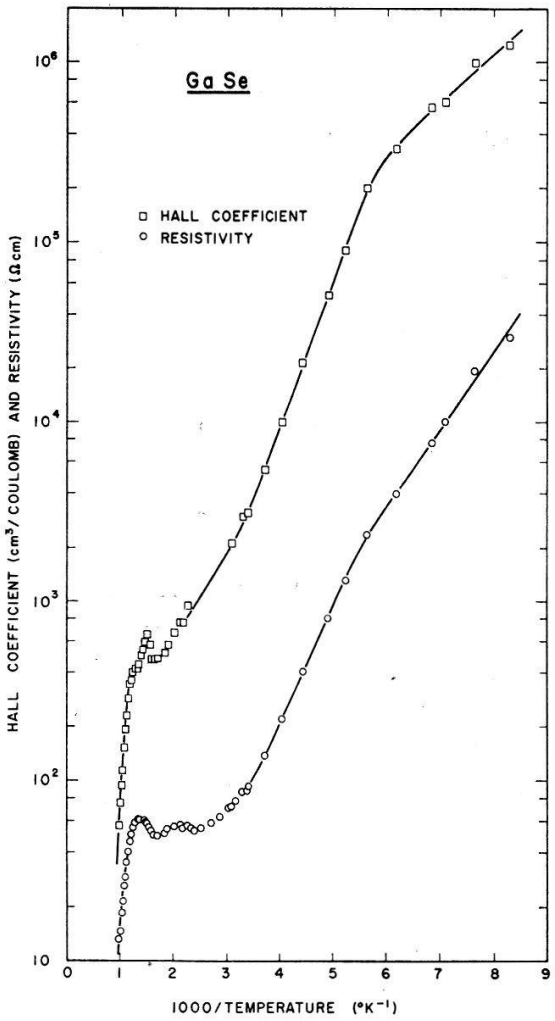

Figure 4

Hall coefficient A_H and resistivity $\varrho_\perp$ of a single crystal of GaSe against the inverse of temperature.

5. Statistics of the Two-Dimensional Band Model

(1) *Density of holes in V_1 and V_2 and electrons in C_4 and C_5*

Let us consider valence band V_2 of Figure 3. The number of holes p_2 in this band may be calculated according to the well-known expression:

$$p_2 \cong 2 \int_{-\infty}^{E_2} D_2(E)\, F(E)\, dE\,. \tag{2}$$

The factor 2 accounts for spin degeneracy, and

$$F(E) = \left[\exp\left(\frac{E_F - E}{k_0\, T}\right) + 1\right]^{-1} \tag{3}$$

is the Fermi-Dirac statistics as it applies to holes, E_F being the Fermi energy and k_0 the Boltzmann constant. $D_2(E)$ is the density of states function. We shall assume bands V_1, V_2, C_4 and C_5 to be isotropic, so that E can be expressed as a monotonic function of the magnitude k of the electronic wave-vector $\boldsymbol{k}$. $D_2(E)$ then takes the simple form:

$$D_2(E) = \left(\frac{dp_2'}{dk}\right)\left(\left|\frac{dk}{dE}\right|\right), \tag{4}$$

where $p_2'(k)$ expresses the number of states within the sphere (or circle in 2 dimensions) of radius k.

For a two-dimensional band structure

$$\frac{dp_2'}{dk} = \frac{1}{4\,\pi^2}\, 2\,\pi\, k = \frac{k}{2\,\pi}\,. \tag{5}$$

It is reasonable to assume band V_2 to be parabolic near the maximum E_2 at $k = 0$. We thus write

$$E_2 - E = \frac{\hbar^2\, k^2}{2\, m_2}\,, \tag{6}$$

and derive a density of states expression independent of E or k:

$$D_2(E) = \frac{m_2}{2\,\pi\,\hbar^2}\,, \quad \text{for } E < E_2\,; \quad D_2(E) = 0\,, \quad \text{for } E > E_2\,. \tag{7}$$

In these expressions m_2 is an effective mass. Equation (2) then becomes

$$p_2 \cong \frac{m_2}{\pi\,\hbar^2} \int_{-\infty}^{E_2} \left[\exp\left(\frac{E_F - E}{k_0\, T}\right) + 1\right]^{-1} dE\,. \tag{8}$$

Unlike the corresponding expression that would obtain in the three-dimensional situation, the integral of (8) can be calculated in closed form. With two substitutions,

$$\alpha_2 = \frac{E_F - E_2}{k_0\, T}\,; \quad \text{and} \quad N_2 = \frac{m_2\, k_0\, T}{\pi\,\hbar^2} \tag{9}$$

one obtains eventually

$$\boxed{P_2 \cong N_2 \ln\left(e^{-\alpha_2} + 1\right)}\,. \tag{10}$$

This expression is interesting because it involves simplifying assumptions with respect to the band structure only, but not with respect to the degree of degeneracy of the statistics; that is to say it is valid for any positive or negative value of α_2. A non-degenerate valence band means

$$\alpha_2 \gg 1\,, \quad \text{and} \quad p_2 \cong N_2\, e^{-\alpha_2}\,, \tag{11a}$$

which has a form familiar in semiconductor physics. A highly degenerate band leads to a more unusual formula:

$$-\alpha_2 \gg 1\,, \quad \text{yields} \quad p_2 \cong -N_2\, \alpha_2\,. \tag{11b}$$

We should like to point out that formulae (10) to (11b) give the hole density in V_2 per unit area of the two-dimensional conductor, or in other words, per cm^2 of one layer.

Formulae similar to (11a) and (11b) hold for bands V_1, C_4 and C_5, but since the last two of these bands have two minima, at C and C', the substitutions for the effective mass m_2 have to be respectively m_1, $2\,m_4$ and $2\,m_5$.

(2) *Density of electrons in band* C_3

Before attempting to evaluate the number n_3 of electrons in band C_3 we shall make some assumptions about the structure of this band. We assume that lines of constant energy run parallel to the sides of the hexagonal zone boundaries of Figure 2. These lines then form a pattern of concentric hexagons within each zone. In directions perpendicular to the zone boundaries, for example OS, we assume the energy to depend quadratically upon the distance Δk from the boundary, and we describe this quadratic dependence with an effective mass m_3.

$$E - E_3 = \frac{\hbar^2(\Delta k)^2}{2\,m_3}\,. \tag{12}$$

In terms of the effective mass, then, we have assumed that it is infinite in directions parallel to the zone boundaries.

With the foregoing assumption the number dn_3' of electronic states between two hexagons of side l separated by an interval dk is given by

$$dn_3' = \frac{6\,l}{4\,\pi^2}\,dk\,. \tag{13}$$

Since the only states that come into consideration are those of lowest energy, lying along the zone boundaries, the length l is, for all present purposes, equal to the distance CC' of Figure 2. Our primitive cell being a rhombus of side a, this distance is equal to $4\,\pi/3\,a$. Combining equations (12) and (13), where dk means $d(\Delta k)$, we obtain for the density of states function $D_3(E)$ of band C_3:

$$D_3(E) = \frac{dn_3'}{dE} = \frac{\sqrt{2\,m_3}}{\pi\,\hbar\,a}\,(E - E_3)^{-1/2}\,. \tag{14}$$

The number of electrons in C_3 then is

$$n_3 \cong 2 \frac{\sqrt{2\, m_3}}{\pi \hbar\, a} \int_{E_3}^{\infty} \frac{(E - E_3)^{-1/2}\, dE}{\exp\left(\frac{E - E_F}{k_0\, T}\right) + 1}. \tag{15}$$

The integral of this expression cannot be evaluated in closed form. However, for p-type material the exponential in the denominator is always very much larger than unity, so that (15) then becomes

$$\boxed{n_3 \cong 2 \frac{\sqrt{2\pi\, m_3\, k_0\, T}}{\hbar\, a}\, e^{-(E_3 - E_F)/k_0 T}}. \tag{16}$$

(3) *Intrinsic behaviour*

If we consider only bands V_2 and C_3 neutrality requires that in the intrinsic range

$$p_2 = n_3. \tag{17}$$

With (11a) and (16) we derive

$$E_F \cong \frac{E_2 + E_3}{2} - \frac{k_0\, T}{4} \ln \frac{8\, \pi^3\, \hbar^2\, m_3}{a^2\, k_0\, T\, m_2^2}. \tag{18}$$

It is easy to convince oneself that E_F decreases with temperature. Equation (18) finally gives, when put back into (11a) or (16):

$$p_2 \cong n_3 \cong \left(\frac{8\, m_2^2\, m_3\, k_0^3\, T^3}{\pi\, \hbar^6\, a^2}\right)^{1/4} e^{-\Delta E/2 k_0 T} \tag{19}$$

where $\Delta E = E_3 - E_2$ is the energy gap.

(4) *Extrinsic range*

At low temperature our GaSe is p-type. We shall therefore assume that we have N_a acceptors of an energy E_a. We shall, however, also assume a certain degree of compensation K, that is N_d donors at an energy E_d such that

$$0 < K = \frac{N_d}{N_a} < 1. \tag{20}$$

The number n_a of electrons in the acceptor sites is

$$n_a = \frac{N_a}{\exp\left(\frac{E_a - E_F}{k_0\, T}\right) + 1}. \tag{21}$$

In the extrinsic range the Fermi level is far below E_d and E_3 so that donors and conduction band can be considered empty. The neutrality condition then requires

$$n_a = p_2 + N_d. \tag{22}$$

In the high temperature limit of this approximation $n_a \cong N_a$ and we derive

$$p_2 \cong N_a\,(1 - K). \tag{23}$$

This condition prevails at temperatures below the intrisic range for which $(E_F - E_a) \gtrsim 4\, k_0\, T$. On the low temperature side one can write $p_2 \ll N_d < N_a$, and derive at once

$$E_F \cong E_a - k_0\, T \ln\left(\frac{1-K}{K}\right) \tag{24}$$

and

$$p_2 \cong N_2 \left(\frac{1-K}{K}\right) e^{-(E_a - E_2)/k_0 T}. \tag{25}$$

We should note that E_F decreases with T for $K < 1/2$ and increases for $K > 1/2$. The significant feature of (25) is the exponent, which has twice the value pertaining to uncompensated material.

When compensation is small, $K \ll 1$, one can show that there is an intermediate range of temperature where (24) and (25) are to be replaced by:

$$E_F \cong \frac{E_2 + E_a}{2} - \frac{k_0\, T}{2} \ln\left(\frac{N_2}{N_a}\right), \tag{26}$$

$$p_2 \cong \sqrt{N_2\, N_a}\, e^{-(E_a - E_F)/2 k_0 T}. \tag{27}$$

In the limit of vanishing compensation, $K = 0$, these last two formulae cover the entire low temperature part of the extrinsic range.

6. Comparison With Experiments

We have mentioned already the agreement between the broad predictions of our band model and available experimental data. We shall attempt to carry the comparison between experiment and theory a step further and point to certain difficulties that such a comparison involves.

(1) *Optical absorption*

The absorption spectra of GaSe and GaS, shown in Figures 5 and 6, are relatively simple. At energies above the edges the absorption coefficient K has a low value of about 10^3 cm^{-1}. In the same energy range we see that K increases when temperature increases, particularly above 150° K. These two properties are generally typical of indirect transitions. The two spectra are, nevertheless, remarkably different. The rate of increase in absorption vs. energy is extremely large for GaSe and very small for GaS. The edge extends over close to 1 eV for GaS and a mere 0.05 eV for GaSe. In addition there is a very strong line structure in the edge of GaSe and a very weak structure, visible only at low temperatures, in the edge of GaS. Although we quoted evidence that a similar line structure found in GaTe is not of an excitonic nature (Brebner *et al.* 1962) we have now reason to believe that the lines found in the absorption spectra of GaTe, GaSe and GaS may be produced by the creation of excitons.

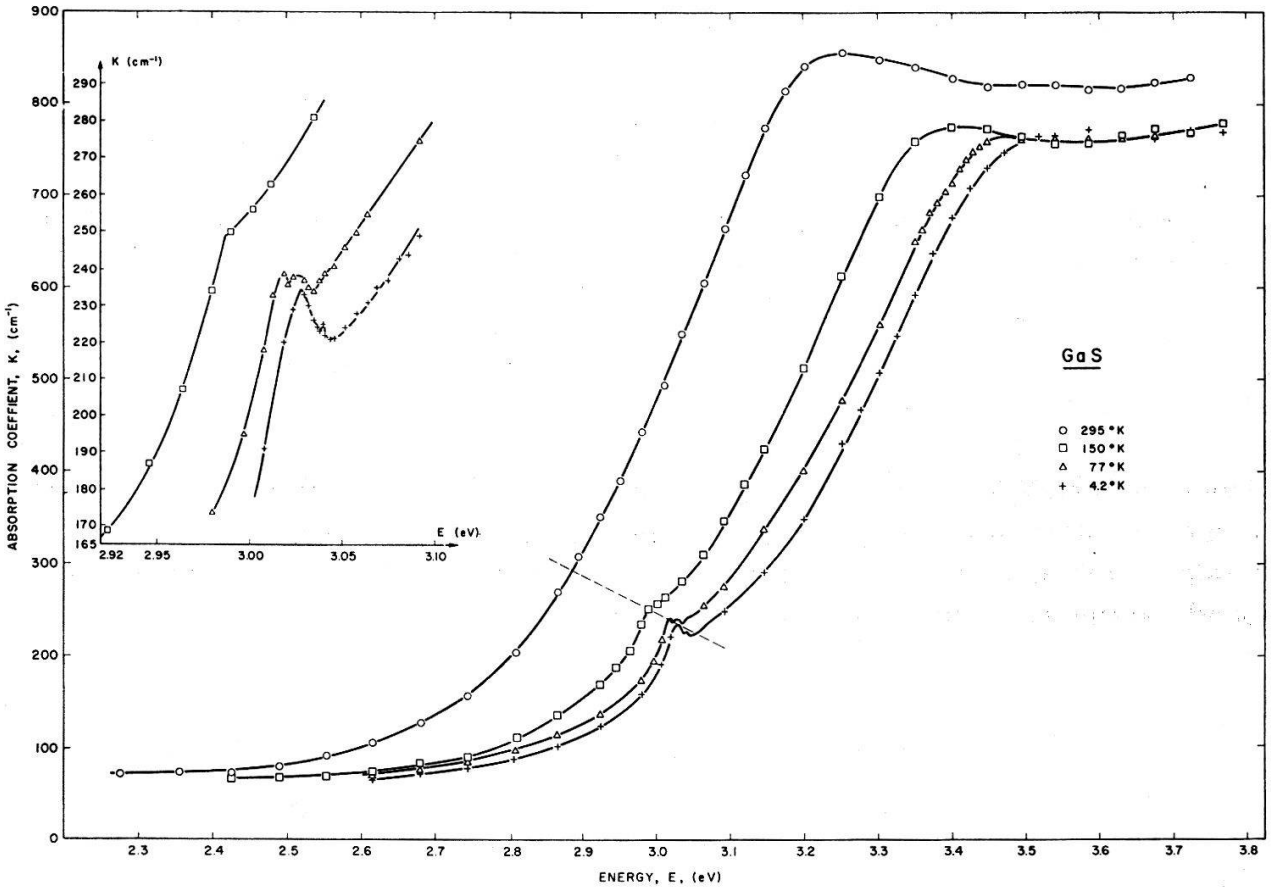

Figure 5

Optical adsorption coefficient of a GaS single crystal at temperatures of 295, 150, 77 and 4.2° K. Unpolarized radiation incident normal to the layers of a 74,5 microns thick crystal.

For the band structure of Figure 3 the edge is likely to arise by the superposition of several types of indirect transitions all involving similar energies. Transitions between two isotropic and parabolic bands, for which the density of states functions were found to be constant (e.g. (7)), yield an absorption coefficient α linearly dependent on the photon energy $E = h\nu$. For example transitions from band V_1 to band C_4 give (c.f. for example SMITH 1959)

$$\alpha_{14e} = \begin{cases} 0 & \text{for } h\nu \leqslant E_4 - E_1 + E_k \\ A_{14e}(h\nu - E_4 + E_1 - E_k) & \text{for } h\nu \geqslant E_4 - E_1 + E_k \end{cases}. \tag{28}$$

In this formula A_{14e} is a constant which depends on the transition probability and the phonon distribution, while the index e signifies that the transition involves emission of a phonon of appropriate wave-vector $\boldsymbol{k}$ and having an energy E_k. Equation (28) only holds for a limited range of positive values of the argument $(h\nu - E_4 + E_1 + E_k)$. For large values of the argument the absorption coefficient generally levels off and eventually diminishes, in a way dependent upon the band shapes. α_{14e} refers to a specific type of phonon and the various acoustical and optical modes of vibration of the lattice will each contribute an absorption coefficient similar to α_{14e}. Since the

transitions can also take place by phonon absorption there will be terms of the type α_{14a}:

$$\alpha_{14a} = \begin{cases} 0 & \text{for } h\nu \leqslant E_4 - E_1 - E_k \\ A_{14a}(h\nu - E_4 + E_1 + E_k) & \text{for } h\nu \geqslant E_4 - E_1 - E_k \end{cases}. \tag{29}$$

Transitions from an isotropic and parabolic band, like valance band V_1, to a band like C_3, the density of states function of which we assumed to be given by (14), leads to absorption coefficients β of another type. For example:

$$\beta_{13e} = \begin{cases} 0 & \text{for } h\nu \leqslant E_3 - E_1 + E_k \\ B_{13e}(h\nu - E_3 + E_1 - E_k)^{1/2} & \text{for } h\nu \geqslant E_3 - E_1 + E_k \end{cases}. \tag{30}$$

The edge therefore arises through the super-position of several terms of both types α and β. In addition a line spectrum may be superposed on the edge. Thus it is not a straightforward matter to determine the energy gap $\Delta E = E_3 - E_2$, or any other band parameter, from the measured absorption spectrum.

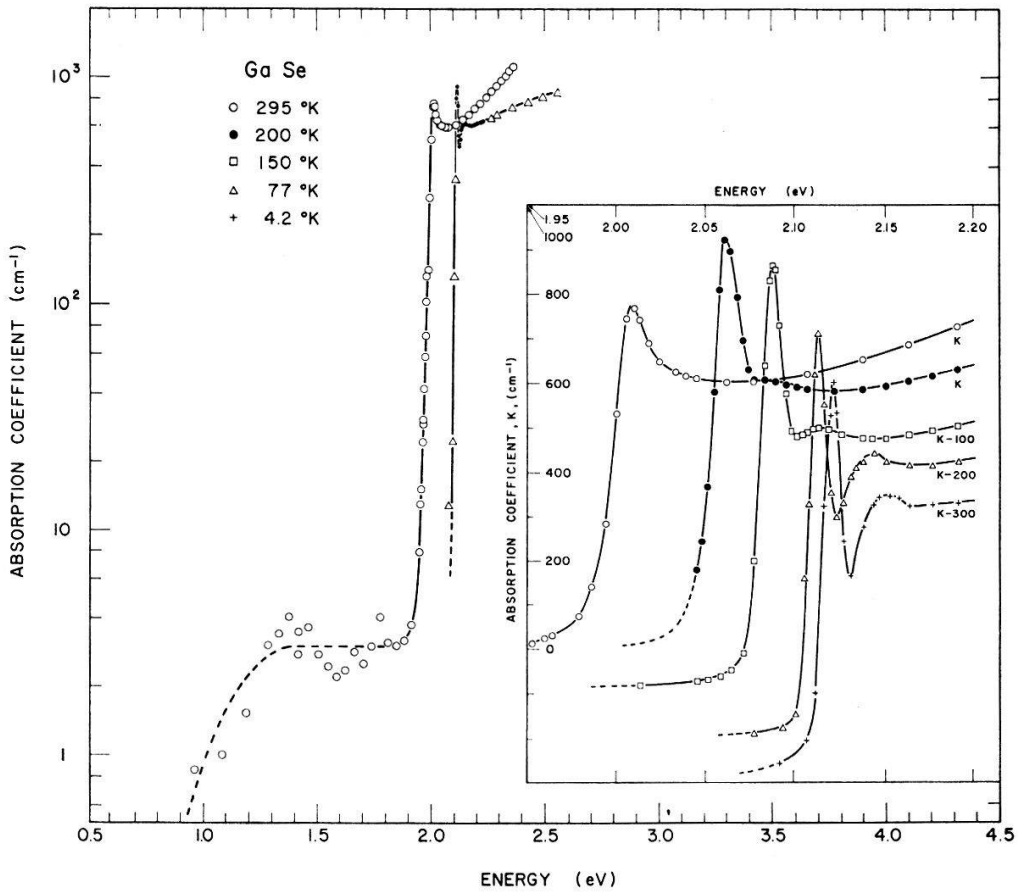

Figure 6

Optical absorption coefficient of GaSe single crystals at temperatures of 295, 200, 150, 77 and 4,2° K. Unpolarized radiation incident normal to the layers of the crystals. Thickness of crystals 275 and 33 microns*).

*) *Note added in proof:* Above 2.5 eV we have found that the absorption increases sharply, exhibiting several edges. This is in contrast with measurements published earlier where a constant absorption had been observed, but resulted from a crack in the sample which developed at low temperature (Brebner and Fischer 1962).

The absorption spectra of Figures 5 and 6 show essentially only a single edge and a line structure. From the sharpness of the edge in GaSe we conclude that it is the fundamental edge that arises from transitions between bands V_2 and C_3 only, and that all other bands are energefically well separated from these two. The sharpness of the edge also suggests that band C_3 is according to the full line of Figure 3 between C and C', so that the absorption would obtain the sharpness of type β. In GaS, however, the edge extends over such a large range of energies that we must assume this edge to arise from a superposition of band to band transitions of type α, whereby energies within the two sets (E_1, E_2) and (E_3, E_4, E_5) are not very different, and with band C_3 following the dashed curve between C and C' of Figure 3. Such a superposition of linear terms α will tend to appear as a quadratic edge, viz. $K \propto (E - \Delta E)^2$. We shall attempt now to determine the energy gaps ΔE of the two substances from their absorption spectra. In the case of GaS we have plotted $K^{1/2}$, K and K^2, where K is the experimental absorption coefficient at 295° K, against the photon energy $E = h\nu$. We found that $K^{1/2}(E)$ approaches a straight line over much the largest range of E values and extrapolates to zero at 2.49 ± 0.02 eV. Extrapolations from the K and K^2 plots intercept the abscissa at 2.76 and 2.95 eV respectively. Since BUBE and LIND (1960) report a sharp maximum in the room temperature photo-conductive response at 2.58 eV, we believe this values to be a reliable estimate of the energy gap ΔE. To obtain a measure of the variation with temperature of ΔE we have assumed it to vary in proportion to the energy $E_{1/2}$ for which the absorption coefficient reaches half its maximum value. Figure 7 is a graph of the values so derived. An alternative derivation of ΔE vs. temperature is given elsewhere (BREBNER and FISCHER 1963).

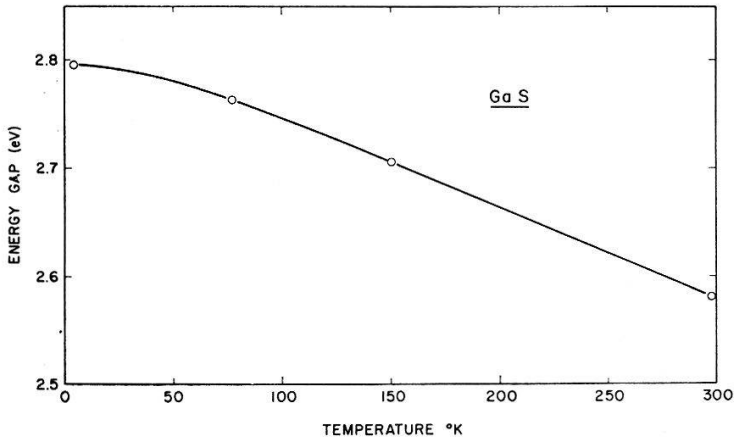

Figure 7
Temperature dependence of the energy gap of GaS.

In the spectra of GaSe (Figure 6) the line structure appears to cover a larger range of energies than the width of the absorption edge. In the absence of a detailed knowledge about the origin of the lines it is not possible to derive an accurate value for the energy gap ΔE. Figure 8 is a plot against temperature T of the three energies $E(K)$ for which the absorption coefficient K is (1) equal to 500 cm^{-1}, (2) is maximum, and (3) is minimum between the two lines. The three curves obtained are practically parallel

and give, we believe, a good measure of the temperature dependence of ΔE. We also think that the actual value of ΔE is comprised between the lowest and uppermost curves of Figure 8.

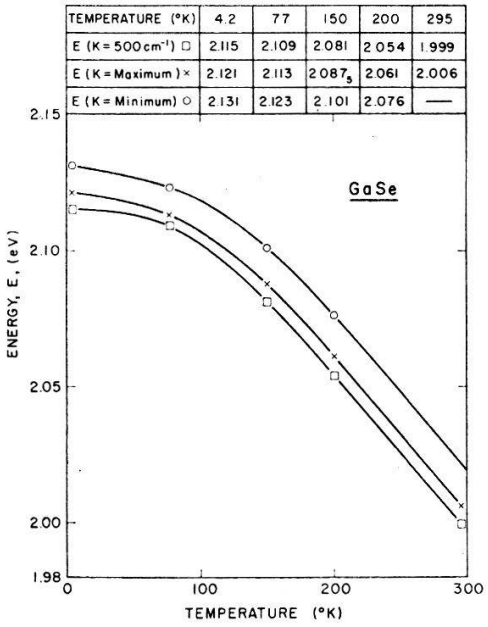

Figure 8

Variation with temperature of the position of the line structure observed in the absorption spectrum of GaSe. The central curve also describes, with an accuracy of $\pm$ 0.02 eV, the behaviour of the energy gap of GaSe.

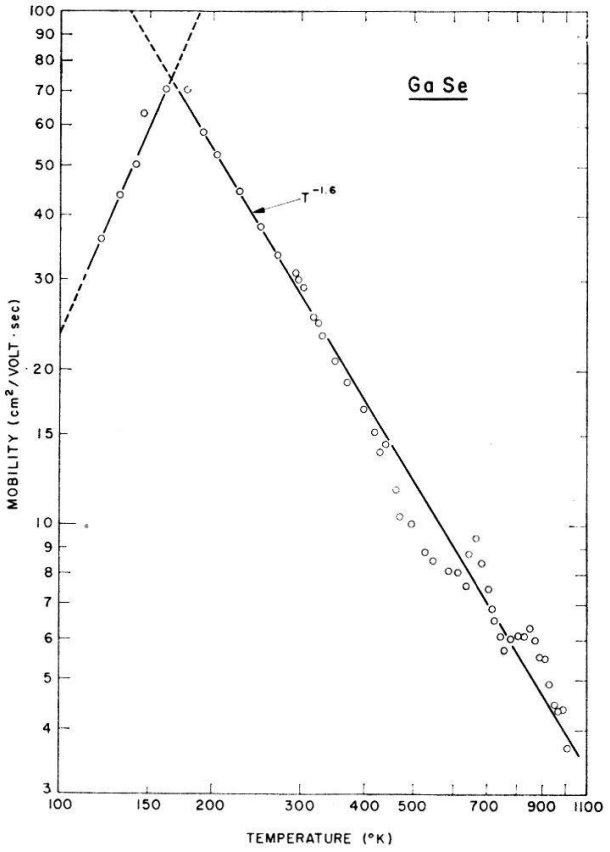

Figure 9

Temperature dependence of the mobility of holes in GaSe in direction parallel to the layers.

(2) *Resistivity and Hall effect*

Resistivity, $\varrho_\perp$, and Hall effect, A_H, of a single GaSe crystal have been measured between 120 and 1000° K and are plotted in Figure 4. The experimental method is described elsewhere (FISCHER and BREBNER 1962). The curves on Figure 4 refer to conduction parallel to the layers ($\perp$ to c-axis) and the hole mobility, μ_p, derived with formula (31) is shown in Figure 9.

$$\mu_p = \frac{8}{3\pi} \frac{A_H}{\varrho_\perp}. \tag{31}$$

It must be said that the coefficient $8/3\pi$ in the above formula is probably not appropriate to a two-dimensional conductor. The error, however, is not likely to exceed 10%. It is also worth noticing that at high temperatures the mobility varies as $T^{-1.6}$, a behaviour typical of thermal scattering in three dimensional crystals. We would not, a priori, expect the same power law to hold for the mobility within a single layer.

We should like to derive effective mass parameters from the Hall effect curve. The available experimental data is too scarce, however, to warrant much detailed calculations. Experiments with systematically doped material should be undertaken before attempting to use the formulae derived in section 5. Let us nevertheless consider the intrinsic behaviour at 1000° K. The density of electrons and holes are then equal and, we shall assume, given by equation (19). To obtain ΔE at 1000° K we extrapolate the upper curve of Figure 4. Equation (19) finally gives:

$$\frac{m_2^2 m_3}{m_0^3} \cong 1.9 \times 10^{-2} \tag{32}$$

which is a reasonable value. We should like to recall that this result is derived under the assumption that band C_3 is of the special non-isotropic shape discussed in section 5. Had we assumed C_3 to have a single minimum with an isotropic and parabolic mass m_3' we would have derived under otherwise similar conditions,

$$\frac{m_2 m_3'}{m_0^2} = 6.7 \tag{33}$$

a result much less plausible than (32).

The extrinsic Hall coefficient of our GaSe sample shows a rather complex behaviour which, in the absence of more experimental data, we do not know whether to explain by a single sort of impurity level and the band structure proposed, or by several kinds of impurity level.

7. Excitons in Layer Structures

It would at first appear that the formation of excitons should be more restricted in a layer crystal because of the restriction of motion into only two dimensions imposed on the charge carriers. We think that this condition provides, on the contrary, for a new mechanism of exciton formation. In analogy with the kind of exciton found in three dimensional crystals the interaction of electrons and holes within one layer leads to allowed states for electron-hole pairs, the energy W_{ex}^n of which is smaller than the

sum of the energies of the unpaired electron and hole of corresponding wave vectors. This comes about because the 'one-electron' approximation neglects direct coulomb interaction between single electrons and holes and the electron hole pairing into excitons arises as a perturbation of the 'one-electron' approach. In the case of layer structures it is possible to imagine that an electron-hole pair, with one particle in each of two adjacent layers, will also bring about a lowering of the energy of the two particles by formation of an excitonic state. This second type of exciton, which one might call 'transverse exciton', may well occur with very much greater probability than the first type which, in opposition, one might label 'longitudinal exciton'. In the state of lowest energy both particles of a 'transverse exciton' are probably at rest, relative motion occurring only in higher excited states. Relative motion between the two partners of a 'longitudinal exciton', however, is always necessary and we think that this important difference may favour the existence of 'transverse excitons' in layer structures.

The origin of the strong lines in the absorption spectra of GaSe and GaTe is still unexplained. Several possible mechanisms may be invoked, in particular exciton formation. If excitons can be created very easily they are likely to have a very long life time. As a consequence the excitonic states are easily saturated and any mechanism that tends to increase the lifetime of the excitons, like annealing, will reduce the strength of the absorption lines. Mechanical working and the accompanying formation of defects which reduce the exciton lifetime should, on the contrary, increase the strength of the lines. The line structure of GaTe appears to behave in this fashion and at first this had been interpreted as evidence against exciton formation (BREBNER *et al.* 1962).

It is interesting to note that GaTe shows two sets of lines (BREBNER *et al.* 1962). There are strong lines in the fundamental edge similar to those found in GaSe. Two more lines at energies of about 2.4 eV are probably of the same nature but arise from transitions involving a lower valence band or higher conduction band.

The line structure in the absorption edge of GaS is much weaker than in the other two compounds. It occurs at energies appreciably higher than the gap (about 0.25 eV above ΔE). This structure has been found at the same energies in materials from a different source by GROSS *et al.* (1959) and may also arise through exciton production.

8. Conclusion

(1) *Band structure of GaS*

With reference to Figure 3, which gives the general outline of the band structure proposed for GaS, we shall rapidly review the parameters which have been determined. At 4.2, 77, and 295° K respectively, the energy gap $E_3 - E_2 = 2.80$, 2.76, and 2.58 eV. The relative accuracy of these figures is about $\pm$ 0.01 eV, the absolute accurary being that of the room temperature figure quoted by BUBE and LIND (1960). We believe $E_2 < E_1$, $E_4 < E_3$, and $E_5 < E_4$, although these differences are probably only of the order of a few tenths of an electron-volt. We also think that the $E(\boldsymbol{k})$ curve along CSC' of wave-vector space is not as constant as indicated by the full line of Figure 3 but varies appreciably, as does for example the dashed line.

(2) *Band structure of GaSe*

The general outline of the band structure proposed for GaSe is also given by Figure 3. However, in contrast to GaS, we believe that $E_1 \neq E_2$, and $E_3 \neq E_4 \neq E_5$, these differences being of the order of half an electron-volt, and we think that $E(\boldsymbol{k})$ along CSC' is nearly constant. At 4.2, 77 and 295°K the band gap $E_3 - E_2$ is respectively about 2.13, 2.12 and 2.02 $\pm$ 0.02 eV.

(3) *General conclusions*

Although rather speculative the method proposed in sections 1 to 3 for the derivation of the band structure of semiconductors with layer structures proved successful in suggesting a band model consistent with known properties of GaSe and GaS. The method may be valid generally when there are no proper chemical bonds between adjacent layers other than for example VAN DER WAALS' bonds. Experimental data help to refine the broad outline derived by the method. The band structure predicts that intrinsic GaSe and GaS is p-type, and subsequent experiments with GaSe confirmed this prediction.

It is proposed that layer structures satisfying the bonding conditions mentioned above favour the existence of a new kind of exciton. The electron and hole of this exciton would be in adjacent layers and the name 'transverse exciton' is therefore suggested, 'longitudinal excitons' then having both electron and hole in the same layer.

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