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Ternary Semiconducting Compounds with Chalcopyrite-Type Structure

I. Fundamental Equation and Its Physically Acceptable Solutions

By

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The equation (1/4) $(c/a)^2 = -\sigma^2 + 2\alpha\sigma - 2$, which relates all structural parameters for the ternary ABC_2 semiconductors with chalcopyrite structure, is analysed (c and a are the tetragonal lattice constants, $\sigma = 4x - 1$, x = fractional coordinate of C atom, $\alpha = (d_{AC}^2 + d_{BC}^2)/(d_{AC}^2 - d_{BC}^2)$, d_{AC} and d_{BC} are the A–C and B–C bond distances, respectively). The analysis gives the following results: 1. For $2.236 > (d_{BC}/d_{AC}) > 0.447$, a chalcopyrite-type structure is not possible. 2. For $0.447 < (d_{BC}/d_{AC}) < 0.557$ or $1.732 < (d_{BC}/d_{AC}) < 2.236$, $(c/a) < 2$ (tetragonal compression). 3. For $(d_{BC}/d_{AC}) = 0.557$ or 1.732, $(c/a) \leqq 2$. 4. For $0.557 < (d_{BC}/d_{AC}) < 1.732$, $(c/a) \gtrless 2$. 5. For a given d_{BC}/d_{AC} the c/a values are between 0 and $2(2|\alpha| - 3)^{1/2}$ with $|\alpha| > 1.5$.

Die Gleichung (1/4) $(c/a)^2 = -o^2 + 2\alpha\sigma - 2$ wird analysiert, die alle Strukturparameter für die ternären ABC_2-Halbleiter mit Chalkopyrit-Struktur verknüpft (c und a sind die tetragonalen Gitterkonstanten, $\sigma = 4x - 1$, x = Teilkoordinate des C-Atoms, $\alpha = (d_{AC}^2 + d_{BC}^2)/(d_{AC}^2 - d_{BC}^2)$, d_{AC} und d_{BC} sind die A–C- bzw. B–C-Bindungslängen). Die Analyse ergibt folgende Ergebnisse: 1) Für $2{,}236 > (d_{BC}/d_{AC}) > 0{,}447$ ist die Existenz einer Chalkopyritstruktur nicht möglich. 2) Für $0{,}447 < (d_{BC}/d_{AC}) < 0{,}557$ oder $1{,}732 < (d_{BC}/d_{AC}) < 2{,}236$ ist $(c/a) < 2$ (tetragonale Kompression). 3) Für $(d_{BC}/d_{AC}) = 0{,}557$ oder $1{,}732$ ist $(c/a) \leqq 2$. 4) Für $0{,}557 < (d_{BC}/d_{AC}) < 1.732$ ist $(c/a) \gtrless 2$. 5) Für ein vorgegebenes d_{BC}/d_{AC} liegen die c/a-Werte zwischen 0 und $2(2|\alpha| - 3)^{1/2}$ mit $|\alpha| > 1.5$.

1. Introduction

Many of the ternary $A^IB^{III}C_2^{VI}$ or $A^{II}B^{IV}C_2^V$ semiconducting compounds crystallize in the chalcopyrite structure (tetragonal, $1\bar{4}2d$, D_{2d}^{12}, No. 122) with distorted tetrahedral CA_2B_2 units. Some of its physical properties depend to some extent on the values of the crystal axis ratio (c/a) and the position x of the C atom. The possibility of correlating fundamental physical properties with structural parameters, led some authors [1, 2] to search for a physical model from which the parameters could be predicted. It has been pointed out by Abrahams and Bernstein [2] that the $A^{II}B^{IV}C_2^V$ with chalcopyrite structure present regular BC_4 tetrahedra; however, it is known that some of them have a structure slightly different from this model [3]. The situation for the $A^IB^{III}C_2^{VI}$ is not so simple. It is worthwhile to have a deeper look into the chalcopyrite structure.

2. Chalcopyrite-Type Crystallographic Structure

Two dimensionless parameters namely,

$$\tau = 2 - \frac{c}{a}, \tag{1}$$

$$\sigma = 4x - 1, \tag{2}$$

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are used to characterize the crystal lattice and its departure from the lattite expected by superposition of two zincblende-type unit cells ($c = 2a$, $x = 1/4$). The parameter τ takes into account the enlargement or compression along the z-axis, σ shows the C-atom displacement from $x = 1/4$, and can be exressed as

$$\sigma = \frac{4}{a^2}\left(d_{AC}^2 - d_{BC}^2\right), \tag{3}$$

where d_{AC}^2 and d_{BC}^2, the squares of A–C and B–C distances in the distorted tetrahedral CA_2B_2 units (Table 1), are given by

$$d_{AC}^2 = a^2\left[x^2 + \left(\frac{1}{4}\right)^2 + \left(\frac{1}{8}\right)^2\left(\frac{c}{a}\right)^2\right], \tag{4}$$

$$d_{BC}^2 = a^2\left[\left(\frac{1}{4}\right) - x + x^2 + \left(\frac{1}{4}\right)^2 + \left(\frac{1}{8}\right)^2\left(\frac{c}{a}\right)^2\right]. \tag{5}$$

Table 1

Positional coordinates of the A, B, and C atoms of the CA_2B_2 tetrahedral unity in chalcopyrite structures

atom	fractional coordinates		
	x	y	z
A_1	0	0	0
A_2	0	1/2	1/4
B_1	1/2	0	1/4
B_2	1/2	1/2	0
C	x	1/4	1/8

Fig. 1 shows the different lattice distortions observed in the ABC_2 chalcopyrite semiconductors.

Combination of equations (2), (4), and (5) leads, after some rearrangement, to

$$\frac{1}{4}\left(\frac{c}{a}\right)^2 = -\sigma^2 + 2\sigma\,\frac{1 + \left(\frac{d_{BC}}{d_{AC}}\right)^2}{1 - \left(\frac{d_{BC}}{d_{AC}}\right)^2} - 2\,. \tag{6}$$

If α is defined by

$$\alpha = \frac{1 + \left(\frac{d_{BC}}{d_{AC}}\right)^2}{1 - \left(\frac{d_{BC}}{d_{AC}}\right)^2}, \tag{7}$$

equation (6) can be written as follows:

$$\frac{1}{4}\left(\frac{c}{a}\right)^2 = -\sigma^2 + 2\alpha\sigma - 2\,. \tag{8}$$

Expression (8) relates all important structural parameters of the ternary chalcopyrite semiconductors. Let us examine physical acceptable solutions of (8). We are interested

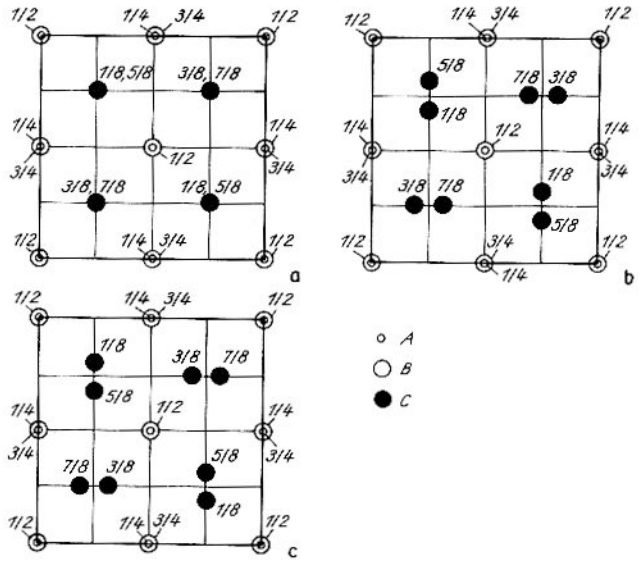

Fig. 1. 001 projection of tetragonal $I\bar{4}2d$ unit cell for ternary chalcopyrite-type crystals. a) No lattice distortion, $\sigma = 0$, $d_{BC} = d_{AC}$. b) Positive lattice distortion, $\sigma > 0$, $d_{BC} < d_{AC}$. c) Negative lattice distortion, $\sigma < 0$, $d_{BC} > d_{AC}$

in those with the following properties: a) c/a and d_{BC}/d_{AC} are real positive numbers; b) $-1 \leqq \sigma \leqq 1$. The latter condition comes from the possible x values for the d positions (Wyckoff notation) of the $I\bar{4}2d$ space group ($x = 0$, $\sigma_{min} = -1$; $x = 1/2$, $\sigma_{max} = 1$). The σ given by equation (8) are

$$\sigma = \alpha \pm \left\{\alpha^2 - \left[2 + \frac{1}{4}\left(\frac{c}{a}\right)^2\right]\right\}^{1/2} . \tag{9}$$

For real σ-values the following condition must be obeyed:

$$\left(\frac{c}{a}\right)^2 \leqq 4(\alpha^2 - 2) . \tag{10}$$

Fig. 2 shows as a dashed line the plot of c/a versus d_{BC}/d_{AC} values that satisfy the condition of equality in (10). The allowed (d_{BC}/d_{AC}, c/a) quadrant is divided in two regions: One with complex, and the other with real σ-values. In the latter region the following requirements are also met:

$$\sigma\,(+) \quad \text{if} \quad \alpha\,(+)\,, \tag{11}$$

$$\sigma\,(-) \quad \text{if} \quad \alpha\,(-), \tag{12}$$

and

$$2^{1/2} \geqq \alpha \geqq -2^{1/2} . \tag{13}$$

Conditions (11) and (12) allow to write (8) in terms of $|\sigma|$ and $|\alpha|$,

$$\frac{1}{4}\left(\frac{c}{a}\right)^2 = -|\sigma|^2 + 2\,|\alpha|\,|\sigma| - 2 \tag{14}$$

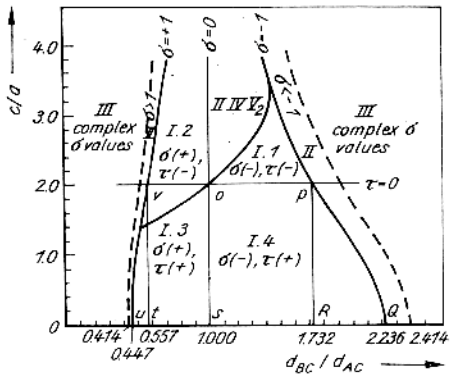

Fig. 2. First quadrant (d_{BC}/d_{AC}, c/a) showing the sections of complex and real σ values. Section I is the region of acceptable solutions ($-1 \leqq \sigma \leqq 1$). In Section II, σ is real but $|\sigma| > 1$. In III, σ is complex. The upper surface, I.1 enclosed by lines $\sigma = -1$, OP, and $\sigma = 0$, has both σ and τ, negative. The OPQS trapezoid, I.4, has negative σ value and positive τ value. In I.3 region (OSUV trapezoid), both σ and τ are positive. The upper surface I.2, is enclosed by lines $\sigma = 1$, VO, and $\sigma = 0$, and has positive σ and negative τ value. VOP line divides section I in two parts: the upper segment which is the region of tetragonal expansion and the bottom one, of tetragonal compression

which can be rearranged to

$$(2\,|\alpha| - |\sigma|)\,|\sigma| = \frac{1}{4}\left(\frac{c}{a}\right)^2 + 2\,. \tag{15}$$

The acceptable solutions of equation (15) are those with

$$|\sigma| \leqq 1\,. \tag{16}$$

Introducing requirement (16) into (15) leads to

$$\left(\frac{c}{a}\right)^2 \leqq 4(2|\alpha| - 3)\,, \tag{17}$$

which implies that $|\alpha| \geqq 1.5$ for the well behaved solutions. Fig. 2 shows as a continuous line the plot of c/a versus d_{BC}/d_{AC} values satisfying the condition of equality in (17), and the sections I, II, and III in which the first quadrant is segmented according to the σ-values. When d_{BC}/d_{AC} ratios are considered, the following conclusions can be derived (see Fig. 2):

(i) For $2.236 > (d_{BC}/d_{AC}) > 0.447$, a chalcopyrite-type structure is physically impossible.

(ii) For $0.447 < (d_{BC}/d_{AC}) < 0.557$ (VTU region) or $1.732 < (d_{BC}/d_{AC}) < 2.236$ (PQR surface), the structure presents tetragonal compression ($c/a < 2$, $\tau > 0$).

(iii) If $d_{BC}/d_{AC} = 0.577$ or 1.732 (TV or RP line), either tetragonal compression or no distortion is expected, $\tau \geqq 0$.

(iv) For $0.577 < (d_{BC}/d_{AC}) < 1.732$ τ can have any possible value, $\tau \gtrless 0$.

(v) For a given d_{BC}/d_{AC} ratio, the c/a values are between 0 and $2(2|\alpha| - 3)^{1/2}$ where α is defined by (6). For $d_{BC}/d_{AC} = 1$, the range of allowed c/a values becomes infinite. As $|d_{BC}/d_{AC} - 1|$ increases, the range of allowed c/a ratios decreases.

If we introduce in (8) the x-values given by Abrahams and Bernstein [2],

$$x = 0.5 - \left[\frac{1}{32}\left(\frac{c}{a}\right)^2 - \frac{1}{16}\right]^{1/2}, \tag{18}$$

we get the expression

$$\alpha = \frac{1 + 0.125\left(\frac{c}{a}\right)^2 + 0.5\left[1 - \left(\frac{1}{2}\left(\frac{c}{a}\right)^2 - 1\right)^{1/2}\right]^2}{1 - \left(\frac{1}{2}\left(\frac{c}{a}\right)^2 - 1\right)^{1/2}} \tag{19}$$

obeyed by the ternary $A^{II}B^{IV}C_2^V$ family with regular BC_4 tetrahedra [2]. The d_{BC}/d_{AC} versus c/a curve that satisfy (19) are shown in Fig. 2 as the II IV V_2 line. In these compounds only two quadrants are possible, the I.3 with σ and τ positive, or the I.1 with both σ and τ negative.

To understand the general behavior of the ABC_2 family it is necessary to find, if possible, the general characteristic for both $A^{II}B^{IV}C_2^V$ and $A^{I}B^{III}C_2^{VI}$. We are working on this line and the results will be published shortly.

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