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Résumé. — Une revue rétrospective générale et quelques progrès récents des dispositifs mettant en œuvre des composés ternaires II-IV-V$_2$ et I-III-VI$_2$ à structure chalcopyrite sont présentés.
L'accent principal est mis sur les dispositifs optoélectroniques. Les sujets traités recouvrent les caractéristiques optiques et électroniques, les dispositifs optiques non linéaires mélangeurs de fréquences, les modulateurs électrooptiques, les lasers, les diodes électroluminescentes et les photo-détecteurs.

Abstract. — A review is presented of the general background and recent progress in device application of the ternary chalcopyrite II-IV-V$_2$ and I-III-VI$_2$ compounds. The main emphasis is on devices for optical and quantum electronics. Topics covered include : and electrical optical characte-ristics ; nonlinear optical frequency mixing devices ; electro-optic modulators ; lasers ; light-emitting diodes ; photodetectors.

1. **Introduction.** — It may seem surprising that the first ternary semiconductor device was cons-tructed some 50 years ago ; it was a point-contact diode [1] using mineral chalcopyrite (CuFeS$_2$). The artificial syntheses [2-5] of compounds of both the II-IV-V$_2$ and I-III-VI$_2$ families have led to intensive studies of their physical properties with a particular view to device applications. The large number of ternary compounds with a corresponding variety of properties [6-8] has resulted in the development, over the past 5 to 6 years, of a number of novel devices.

The aim of this paper is to review devices based upon the II-IV-V$_2$ and I-III-VI$_2$ compounds. The primary emphasis will be upon applications in optical and quantum electronics as a large number of labora-tory devices have been demonstrated in this general area. An attempt will be made to assess the competi-veness of ternary devices against those using more conventional materials.

As device application of ternary compounds is still relatively new their most important properties will be surveyed. Excluded from the review, due to limited data, will be II-IV-V$_2$ compounds involving Be, Mg, Ca or Mn(II) and N or Sb(V), and I-III-VI$_2$ compounds with Tl or Fe(III). The Al(III) I-III-VI$_2$ compounds are also rejected as being insufficiently stable for practical devices ; the one exception is CuAlS$_2$ which is the least unstable of the Al compounds and has the largest measured band-gap (direct). Dis-cussion will normally be limited to crystals with the chalcopyrite structure (an ordered super-structure based on sphalerite). Brief mention will be made of two recently investigated compounds, LiInS$_2$ and

LiInSe$_2$, which crystallize with the β-NaFeO$_2$ wurtzite super-structure. The vitreous states of CdSiAs$_2$, CdGeP$_2$ and CdGeAs$_2$ will be excluded from this review.

2. **Electrical characteristics.** — The band struc-tures of chalcopyrite crystals have undergone intensive investigation both theoretically and experimentally. The lower symmetry of chalcopyrite as against spha-lerite leads to greater band complexity and can result in optical transitions which would be forbidden in sphalerite (for $k = 0$), *pseudo-direct* transitions [9]. In tables Ia and Ib measured values of the lowest band-gap are presented together with the nature of the corresponding optical transition. It will be noted that for all the I-III-VI$_2$ compounds for which experimental measurements have been made the lowest gap is direct, as might be expected from the *parent* II-VI compounds. In II-IV-V$_2$ compounds with band-gaps less than or equal to ~ 1.7 eV the transition is direct, while for larger band-gaps it is either pseudo-direct or indirect. A direct transitions with high transition probability (thereby excluding pseudo-direct crystals) is required for efficient luminescence, that is to say for light-emitting-diodes (LED's) and lasers, and is also desi-rable for certain types of photodetector.

Carrier types which can be produced in these compounds are also given in tables Ia and Ib together with the order of magnitude of resistivity if it is low. It will be noted that all the Zn compounds are p-type whereas the Cd compounds, excepting CdSiP$_2$ and CdSiAs$_2$, can be made with both p- and n-type conduc-tivity. All the Cu compounds can be prepared with p-type conductivity and compounds containing In

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TABLE Ia

Electrical characteristics of II-IV-V$_2$ *compounds*
(room temperature)

Ternary	E_g eV	Equiv. λ μm	Transition	Conduction $(\rho, \Omega\,cm)$	
ZnSiP$_2$	2.05	0.61	pseudo-direct	p	n
ZnSiAs$_2$	1.75	0.71	pseudo-direct	p(1)	
ZnGeP$_2$	2.0	0.62	pseudo-direct	p(1)	
ZnGeAs$_2$	1.1	0.91	direct	p	
ZnSnP$_2$	1.65	0.75	direct	p	
ZnSnAs$_2$(*)	0.75	1.65	direct	p	
CdSiP$_2$	2.1	0.59	indirect		n
CdSiAs$_2$	1.55	0.80	direct	p	
CdGeP$_2$	1.7	0.72	direct	p(1)	n(1)
CdGeAs$_2$	0.55	2.25	direct	p(1)	n
CdSnP$_2$	1.15	1.1	direct	p	n(10^{-1})
CdSnAs$_2$	0.26	4.8	direct	p	n

(*) Structure with $\bar{4}$ point group. Magnitude of resistivity ρ only given if $\leqslant 1\,\Omega$ cm.

TABLE Ib

Electrical characteristics of I-III-VI$_2$ *compounds*
(room temperature)

Ternary	E_g eV	Equiv. λ μm	Transition	Conduction $(\rho, \Omega\ cm)$	
CuAlS$_2$	3.5	0.36	direct	p	n
CuGaS$_2$	2.45	0.51	direct	p(1)	
CuGaSe$_2$	1.7	0.74	direct	p(10^{-2})	
CuGaTe$_2$	1.1	1.15	—	p	
CuInS$_2$	1.55	0.80	direct	p	n(1)
CuInSe$_2$	1.0	1.25	direct	n(10^{-1})	n(10^{-1})
CuInTe$_2$	0.95	1.3	—	p	
AgGaS$_2$	2.65	0.47	direct	p(s-i)	n(s-i)
AgGaSe$_2$	1.8	0.69	direct		(s-i)
AgGaTe$_2$	1.3	0.95	direct	p(1)	
AgInS$_2$	1.9	0.65	direct		n
AgInSe$_2$	1.25	1.0	direct		n(10^{-2})
AgInTe$_2$	1.0	1.25	direct	p(1)	n

s-i : semi-insulating. Magnitude of resistivity ρ only given if $\leqslant 1\,\Omega$ cm.

n-type ; thus CuInS$_2$ and CuInSe$_2$ can be made either p- or n-type, and with useful conductivities (there is no systematic work on CuInTe$_2$). For the I-III-VI$_2$ compounds substantial changes in resistivity and even of carrier type can be obtained by annealing the crystals in an excess or deficiency of chalcogen [10]. Thus an excess chalcogen anneal can change n-type crystals to p-type or induce an increase in p-type conductivity ; annealing in vacuum or argon, and possibly with excess cation material [11], can have the reverse effect. These results suggest that intrinsic defects in the I-III-VI$_2$ compounds determine the electrical transport behaviour, Cu or Ag vacancies acting as acceptors and chalcogen vacancies as donors. Particularly deep intrinsic traps in AgGaS$_2$ [12], and possibly also in AgGaSe$_2$, result in crystals which are semi-insulating

[13], $\rho > 3 \times 10^{10}$ Ω.cm. Doping experiments, for both ternary families, have been rather less fruitful although a few successes have been reported, for instance CdSnP$_2$ being converted from p-type to n-type by the addition of Cu [14], and Cd and Zn acting as donors in certain I-III-VI$_2$ compounds [10, 15-17].

Detailed electrical characterisation, involving measurements of carrier concentrations, mobilities, effective masses and activation energies for different doping concentrations and temperatures, has begun only very recently [18-21] and much more work is needed using crystals of high quality, good stoichiometry and with known impurity concentrations. For example, the effect of crystalline imperfections upon mobility needs investigation although it is worth noting that an electron mobility of 20 000 cm^2/VS was reported for CdSnAs$_2$ as long ago as 1962 [22].

3. Optical characteristics. — The $\bar{4}$2m point group of the chalcopyrite structure results in crystals which exhibit linear dichroism and uniaxial birefringence. The latter property is important as it can make *phase-matching* possible in nonlinear frequency mixing devices. Optical activity (and circular dichroism) is also permitted by this point group but is normally masked by linear birefringence [23].

Crystals with the β-NaFeO$_2$ structure, point group mm2, are of course optically biaxial.

3.1 TRANSMISSION. — The basic transmission range of a ternary compound is constrained by the electronic band-edge at short wavelengths and by two-phonon summation bands at long wavelengths [24]. Detailed experimental studies of electronic structure and of lattice vibrations now permit these two absolute limits to be defined with good accuracy, due allowances being made for dichroism and temperature dependences. The whole of the visible, near infrared and medium infrared transmission range, wavelengths 0.4 to 25 μm, is encompassed by the wide variety of ternary compounds available.

Transmission is again possible in the sub-millimetre region beyond the restrahl bands, the high frequency limit at room temperature being determined by two-phonon difference bands and possibly by free-carrier absorption. Both these sources of loss disappear at low temperature leaving the ultimate limit as the wing of the lowest frequency polar lattice band. ZnGeP$_2$ is the only ternary compound for which a submillimetre *transmission* measurement has been made [25]. This showed that at room temperature ZnGeP$_2$ has a useful transmission, loss coefficient $\alpha < 6$ cm^{-1} for wavelengths longer than 100 μm (note : $\alpha < 3$ cm^{-1} is the more usually adopted transmission limit).

For nonlinear optical applications total losses of less than a few cm^{-1} are essential and $\alpha < 0.1$ cm^{-1} is the objective. Within the basic transmission range a number of factors can result in losses. Three-phonon summation bands are fundamental to any crystal and

result in absorption coefficients of ~ 1 cm^{-1}. In p-type material intravalence band transitions can produce substantial absorption ; for instance in CdGeAs$_2$ $\alpha \simeq 1$ cm^{-1} at 5.5 μm for $p \simeq 10^{15}$ cm^{-3} [26]. Free-carrier absorption will arise n-type crystals.

Sources of transmission loss resulting from crystalline inhomogeneity, departures from stoichiometry and presence of impurities are scatter, short-wave shoulders due to band-tailing, and impurity bands. Micron-sized scattering centres, most probably induced by variations in stoichiometry, have been observed for AgGaS$_2$ [27], AgGaSe$_2$ [28] and AgGaTe$_2$ [29]. Twin lamellae [30] have been discovered in a number of ternary compounds and may induce losses.

Five crystals of particular interest for frequency mixing devices have been grown to centimetre dimensions and low losses achieved by careful control of stoichiometry and annealing techniques. The minimum infrared losses achieved are ~ 1 cm^{-1} for ZnGeP$_2$ [31], ~ 0.25 cm^{-1} for CdGeAs$_2$ [32], ~ 0.1 cm^{-1} for AgGaS$_2$ [33] and LiInS$_2$ [34] and ~ 0.05 cm^{-1} for AgGaSe$_2$ [35].

3.2 DISPERSION. — Refractive indices have been measured over wide wavelength ranges for a total of 13 ternary compounds, 11 having chalcopyrite structure [31, 36-41], and LiInS$_2$ [34] and LiInSe$_2$ [42] with β-NaFeO$_2$ structure. Accurate values of refractive index are required to determine phase-matching conditions in frequency mixing, see section 3.3, as birefringence must then exactly balance dispersion. Variations in crystalline stoichiometry can have significant effects upon refractive index and birefringence [41, 43, 44] as can have intra-valence band transitions in p-type crystals [32].

For interpolation between experimentally measured index values Sellmeier expressions are the most useful as well as having a sound physical basic. Two contributions to dispersion must be allowed for, electronic and lattice.

Wemple and DiDomenico [45, 46] have shown that for compounds belonging to a common family the *electronic* contribution to dispersion has a simple form. Starting from the equation

$$n^2 = 1 + \frac{F}{E_0^2 - (hc/\lambda)^2}$$

where E_0 is a single resonance energy averaging over all bands, they defined a *dispersion energy*

$$E_d = F/E_0$$

and which is essentially constant within a compound family. Extending this approach to ternary compounds [47] gives for the II-IV-V$_2$ family $E_d = 36 \pm 1$ eV, very close to the value of 35 eV for III-V compounds, and for the I-III-VI$_2$ family $E_d = 24 \pm 2$ eV to be compared to 26 eV for II-VI compounds. One model used to explain [45, 46] the invariability of E_d

considers the electronic absorption to be characterised by a constant value of conductivity ranging from E_g (the lowest band-gap) to $b \times E_g$, where $b = 3.4$ for covalent compounds. It is simple to show that this model predicts

$$E_0 \simeq \tfrac{1}{2}(E_g + E_G)$$

where E_G is the *dielectric energy gap* [48]. For the two ternary families the above equation has an error of less than $\pm$ 10 %. Since E_g can be found experimentally and E_G calculated [49, 50] the electronic contribution to dispersion can be estimated for a compound for which the indices are as yet unmeasured.

The lattice contribution to dispersion can be represented by a term

$$+ \frac{D}{1 - (\lambda_R/\lambda)^2}$$

where λ_R is a *centre of mass* restrahl wavelength which need not be known that accurately since transmission stops at $\lambda_R/2$. The oscillator strength D is reasonably constant within a ternary family.

It is of interest to construct, using the above results, a Sellmeier expression for AgGaTe$_2$ as this compound has a transmission spanning the whole of the medium infrared (see Table II). Thus

$$n^2 = 1 + \frac{7.13}{(1 - 0.137/\lambda^2)} + \frac{1.85}{(1 - 2\,400/\lambda^2)}$$

where λ is in μm. For second harmonic generation from 10.6 μm to 5.3 μm the predicted dispersion is then + 0.185 and the birefringence of AgGaTe$_2$ must have a magnitude larger than this for phase-matching.

3.3 NONLINEAR PHENOMENA. — The expression

$$P = \varepsilon_0(\chi_I : E + \chi_{II} : EE + \chi_{III} : EEE + \ldots)$$

is the foundation of nonlinear optics. P is the optical polarisation induced in a medium by the net electric field E, through the linear term $\varepsilon_0 \chi_I$: E and non-linear terms involving field to second — and third — order respectively. The tensor susceptibilities — χ_I, χ_{II}, χ_{III} — are subject to the symmetry of the medium and, in particular, χ_{II} is nonzero only for acentric crystals (i. e. without inversion symmetry). It is important to note that *all* compounds with an adamantine (diamond-like) structure are acentric as a consequence of the two distinct inter-penetrant sub-lattices and will therefore exhibit second-order nonlinear effects [51]. General rules exist for determining whether a given compound will crystallize as an *adamantine* structure [52].

The nonlinear polarisation arising from $\varepsilon_0 \chi_{II}$: EE leads to frequency mixing, generation of the second harmonic (2ω) of a fundamental laser frequency (ω), and sum and difference mixing of two input frequencies. For efficient conversion the propagation vectors

k of the waves in the crystal must satisfy *phase-matching* conditions as follows :

$$\omega_3 \equiv \omega_{SH} = 2\omega_F , \qquad \mathbf{k}_{SH} = \mathbf{k}_F + \mathbf{k}_F ;$$

$$\omega_3 = \omega_2 + \omega_1 , \qquad \mathbf{k}_3 = \mathbf{k}_2 + \mathbf{k}_1 ;$$

and

$$\omega_1 = \omega_3 - \omega_2 , \qquad \mathbf{k}_1 = \mathbf{k}_3 - \mathbf{k}_2 .$$

These conditions reduce to requirements on refractive indices ($|\mathbf{k}| = n\omega/c$) which can only, for frequencies within the basic transmission range, be satisfied if the crystal is birefringent. The highest frequency (ω_3) is then polarized so that it has a low index — n_0 in a positive uniaxial crystal, n_e in a negative uniaxial crystal. The *phase-matching angle* is the angle of propagation to the optic axis at which the extraordinary index, or indices, has the exact value(s) required for the relevant phase-matching condition to be satisfied. Examination of the phase-matching conditions shows that second harmonic generation demands the largest birefringence and that for $\omega_1 \ll \omega_2$ (constant ω_3) a much smaller birefringence can be tolerated.

Third harmonic generation is possible through $\varepsilon_0 \chi_{III}$: EEE with

$$\omega_3 \equiv \omega_{TH} = 3\omega , \qquad \mathbf{k}_{TH} = \mathbf{k}_F + \mathbf{k}_F + \mathbf{k}_F .$$

The need to achieve phase-matching thus places a further requirement upon crystals for frequency mixing devices, namely that they should exhibit birefringence. This is the dominant reason for the nonlinear optical interest in II-IV-V$_2$ and I-III-VI$_2$ chalcopyrite crystals as against III-V and II-VI sphalerite and wurtzite crystals (the birefringence of hexagonal wurtzite crystals is small and phase-matching can be achieved only with CdSe).

Through crystal symmetry there are just three non-zero elements for the second-order susceptibility tensor $\mathbf{d} \equiv \chi_{II}/2$ in the $\bar{4}2m$ point group ;

$$d_{14} = d_{25} \quad \text{and} \quad d_{36} .$$

For frequencies all lying within the basic transmission range of a crystal the polarisation results from displacement of valence electrons and d_{14} then equals d_{36}. Predictions have been made for the second-order electronic susceptibility of ternary chalcopyrite crystals either by *ab initio* molecular orbital calculation [53] or through the *a posteriori* bond charge approach [54-56]. Satisfactory agreement is obtained between calculated and measured nonlinear susceptibilities. A theoretical model also exists for the third-order susceptibility which includes the additional contribution from conduction electrons [57].

Table II summarises the relevant properties of the six ternary compounds which have sufficient birefringence for phase-matching. The short wavelength limit of the working range for certain crystals is determined by phase-matching rather than absorption. The compound AgGaTe$_2$ has yet to be fully characterised [58] as it has proved impossible to grow crystals of the desired quality.

A further nonlinear phenomenon only allowed in acentric crystals is the electro-optic effect. This concerns the change in linear optical properties — as expressed by the impermittivity tensor $\varepsilon_r^{-1}(\omega)$ — of a crystal when it is subjected to a low frequency (relative to restrahl frequencies) electric field, E(0) :

$$\Delta\varepsilon_r^{-1}(\omega) = \mathbf{r} : \mathbf{E}(0) .$$

By crystal symmetry the non-zero elements of the $\bar{4}2m$ electro-optic tensor are $r_{41} = r_{52}$ and r_{63}. There are two distinct values for r, depending upon whether the frequency of the applied field is well above crystal acoustic resonances — $\mathbf{r}^S$ for constant strain, or well

TABLE II

Frequency mixing materials

Ternary	Working range, μm	d_{14}, 10^{-10} m/V	G_d (λ_3, μm)	I_{dam}, MW/cm^2
ZnGeP$_2$	0.9-12, 100-	1.1	0.58 (1.83)	~ 3
CdGeAs$_2$	2.8 -18	4.0	0.58 (5.3)	38
AgGaS$_2$	0.58-13	0.19	0.11 (1.06)	20-25
AgGaSe$_2$	1.0 -18	0.41	0.14 (1.83)	11
ZnSiAs$_2$	1.4 -12	1.1	0.27 (2.7)	—
LiInS$_2$ (*)	0.43-10	0.085 (**)	0.027 (1.06)	—
AgGaTe$_2$	1.4 -23	> 0.8	—	—
Proustite	0.6 -13	0.27 (**)	0.30 (1.06)	20

G_d for $I_3 = 1$ MW/cm^2, $l = 1$ cm.
(*) Point group mm2.
(**) d_{eff}.

TABLE III

Linear electro-optic materials

Ternary	r_{41}, 10^{-12} m/V	r_{63}, 10^{-12} m/V	$\varepsilon_1(0)$	$\varepsilon_3(0)$	n
ZnGeP$_2$ (S)	+ 1.6	− 0.8	15	12	3.15
CuGaS$_2$ (S)	+ 1.1	+ 1.05	9.3	10.0	2.5
AgGaS$_2$	4.0 (T)	3.0 (T)	10 (S)	14 (S)	3.4
GaAs (S, T)	$r_{41} = 1.5 \times 10^{-12}$ m/V		$\varepsilon(0) = 12.5$		$n = 3.3$
	Figure-of-merit = 7.5		Transmission : 1-15 µm		
ZnGeP$_2$	Figure-of-merit = 5.5		Transmission : 0.7-13 µm		

below them — r^T for constant stress. In the latter case dimensional changes arising from the piezo-electric effect contribute to r through the elasto-optic effect.

Measurements of (linear) electro-optic coefficients are very limited for the ternary semiconductors and are summarised in table III. Certain values are available for three chalcopyrite structure crystals [59, 60], for two with β-NaFeO$_2$ structure [61], and for CdGa$_2$S$_4$ [62] which is a defect chalcopyrite.

A fundamental relationship links the frequency mixing and electro-optic tensors when the lowest mixing frequency falls below the restrahl region. Both lattice and electronic displacements then contribute to d. For point group $\overline{4}2m$ this relationship is

$$d_{14}^{\omega_1 \ll \omega_R} = - \frac{n_e^2 \, n_0^2}{4} \cdot r_{41}^S$$

$$d_{36}^{\omega_1 \ll \omega_R} = - \frac{n_0^4}{4} \cdot r_{63}^S \, .$$

These equations can be used in predictions of difference mixing (down-conversion) efficiencies into the sub-millimetre once the electro-optic coefficients have been measured.

3.4 LASER DAMAGE. — In frequency mixing devices the nonlinear crystal is normally exposed to laser radiation of very high power, most frequently pulsed. Damage to the crystal may result, characterised by a threshold power density (power/unit area). The limited data available on laser damage of ternary crystals is summarised in table II for pulses of duration in the range 10 to 100 nanoseconds. Since there are indications that damage threshold increases with crystal quality [32, 37] it is not known whether the values in table II represent those ultimately achievable.

4. Nonlinear optical devices. — 4.1 FREQUENCY MIXING DEVICES. — The five basic types of frequency mixing device are summarised in figure 1 ; all but the third harmonic generator rely upon the second-order nonlinear polarisability of acentric crystals.

The most sophisticated of these devices is the para-

metric oscillator [63], in which a fixed input (pump) frequency is converted into two outputs,

$$\omega_3 \to \omega_2 + \omega_1$$

whose frequencies are controlled, and can thereby be tuned, through phase-matching. A parametric oscillator can be viewed as a laser but with the gain arising from frequency mixing rather than stimulated emission and with, of course, two outputs rather than one. For plane waves the parametric gain

$$G = \frac{2\,\omega_2\,\omega_1\,d_{\text{eff}}^2}{\varepsilon_0\,n_3\,n_2\,n_1\,c^3} \cdot l^2 \cdot I_3$$

where d_{eff} is an effective nonlinear coefficient which takes into account field directions relative to crystallographic axes, l is the length of the crystal and I_3 the pump power density. G not only determines the pump threshold for parametric oscillation (G equal to round-trip losses at ω_2) but is also related to the conversion efficiencies for the other second-order devices, as indicated in figure 1.

A useful figure-of-merit for a frequency mixing crystal is the parametric gain at degeneracy,

$$\omega_2 = \omega_1 = \omega_3/2 \, ,$$

for a crystal 1 cm long, and with a pump power density of 1 MW/cm^2. This quantity G_d is presented in table II for the shortest *practical* pump laser wavelength for which a degenerate oscillator will phase-match in a crystal. It is worth noting that all the pump wavelengths are more than a factor of two larger than the band-edge so that two-photon absorption is avoided. Data is also presented in the table for proustite (Ag$_3$AsS$_3$) as this material has been successfully used in all second-order devices including a parametric oscillater [64]. To date, no parametric oscillator has been reported using on a ternary compound despite a number of optimistic projections. It should be noted that double refraction has been neglected in defining the figure-of-merit. This is justified for infrared nonlinear devices as their operation is constrained by damage and not by available laser pump powers. Pump beams can therefore be used of a diameter large enough to make double refraction walk-off negligible by comparison.
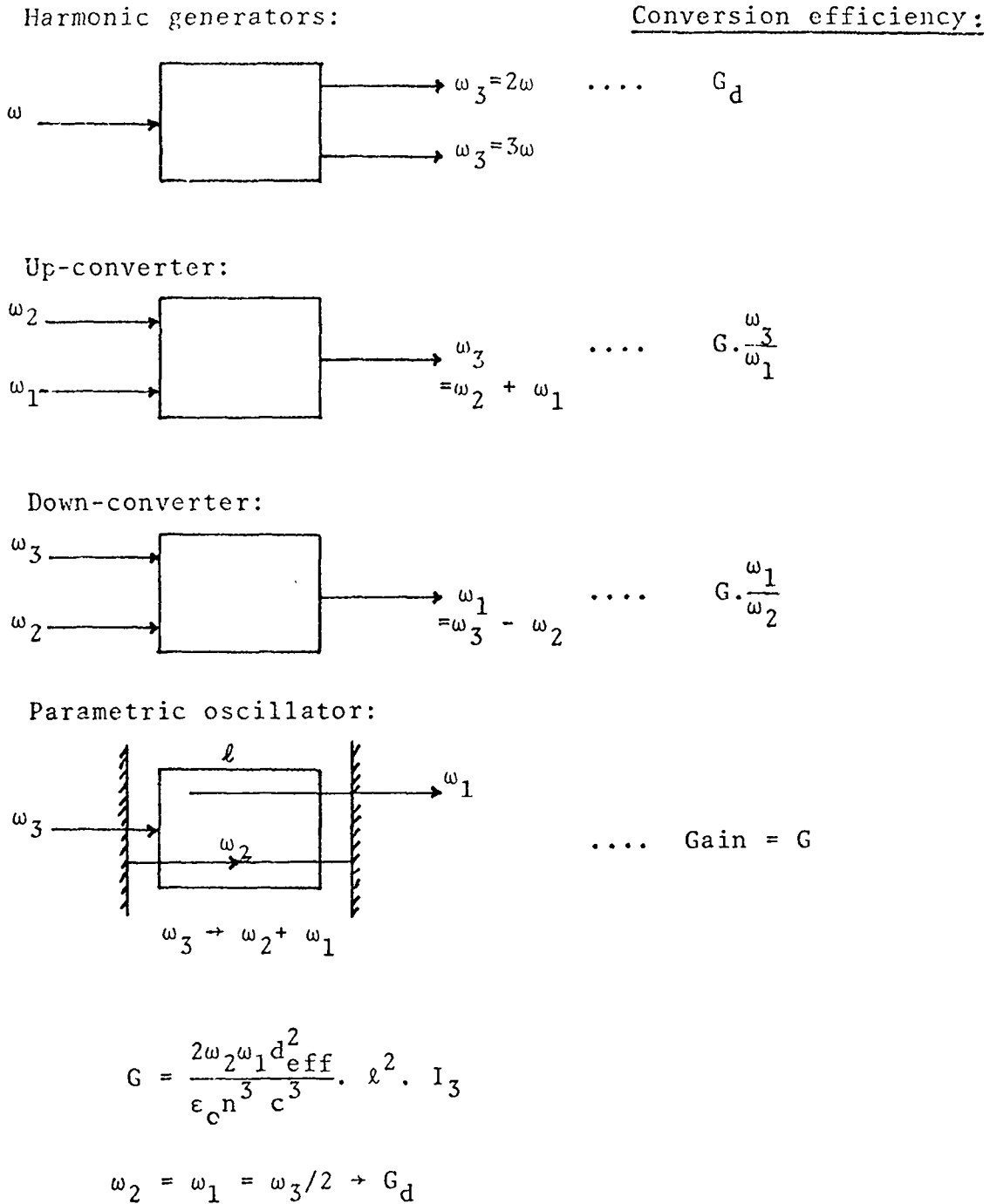
Harmonic generators: <u>Conversion efficiency:</u>

$\omega \longrightarrow$ [ ] $\longrightarrow \omega_3 = 2\omega$ .... G_d

$\longrightarrow \omega_3 = 3\omega$

Up-converter:

$\omega_2 \longrightarrow$ [ ] $\longrightarrow \omega_3$ .... $G \cdot \dfrac{\omega_3}{\omega_1}$

$\omega_1 \longrightarrow$ $= \omega_2 + \omega_1$

Down-converter:

$\omega_3 \longrightarrow$ [ ] $\longrightarrow \omega_1$ .... $G \cdot \dfrac{\omega_1}{\omega_2}$

$\omega_2 \longrightarrow$ $= \omega_3 - \omega_2$

Parametric oscillator:

$\omega_3 \longrightarrow$ [ℓ] $\longrightarrow \omega_1$

ω_2

$\omega_3 \rightarrow \omega_2 + \omega_1$

   ....   Gain = G

$$G = \frac{2\omega_2\omega_1 d_{eff}^2}{\varepsilon_c n^3 c^3} \cdot \ell^2 \cdot I_3$$

$$\omega_2 = \omega_1 = \omega_3/2 \rightarrow G_d$$

FIG. 1. — Frequency mixing devices.

Phase-matched second harmonic generation has been obtained with $AgGaS_2$ [65, 66], $CdGeAs_2$ [31, 32, 37, 39] and $AgGaSe_2$ [35, 67] for 10.6 μm CO_2 lasers, with the maximum peak power conversion at 17 % for $CdGeAs_2$ probably limited by carrier absorption [32]. $AgGaS_2$ has also been used to second harmonic generate the outputs of a parametric oscillator [44]. Reasonably efficient third harmonic generation has also been achieved with $CdGeAs_2$ and efficiencies in excess of $\sim$ 30 % predicted [57]. Harmonic generators are of practical value in providing high power coherent radiation at new wavelengths.

Up-converters have been investigated for two fields of application ; frequency conversion of signals in the medium infrared to the visible-near infrared so as to exploit photomultiplier detection, and for infrared imaging. Only signal up-conversion has been demonstrated with ternary compounds, $AgGaS_2$ [68] and $ZnGeP_2$ [43] being used. Detailed systems studies have also been carried out for up-converters based

on these crystals [69-71]. Developments in conventional infrared devices, of new nonlinear up-conversion processes based upon alkali metal vapours [72] and even of a better nonlinear crystal, ε-GaSe [73, 74] do not suggest a great future for ternary compounds in up-converter applications.

It is in tunable infrared down-converters that the ternary compounds appear to have the greatest promise. AgGaS₂ has been used to generate tunable medium infrared from tunable dye laser inputs [75, 76], the transmission and phase-matchability down to 0.58 μm being central to this approach. LiInS₂ (see Table II) also offers a potential for down-conversion from visible dye lasers. Step-tuned down-conversion from CO and CO₂ lasers has been obtained with AgGaSe₂ [67] and for CdGeAs₂ [32] on a cw basis. AgGaSe₂ has also been used for continuously tuned down-conversion from a fixed frequency laser and tunable parametric oscillator [35] ; wavelengths 7 to 13.5 μm were produced (Fig. 2) and extension to 18 μm is feasible. This particular ternary compound appears attractive for a variety of down-conversion schemes.
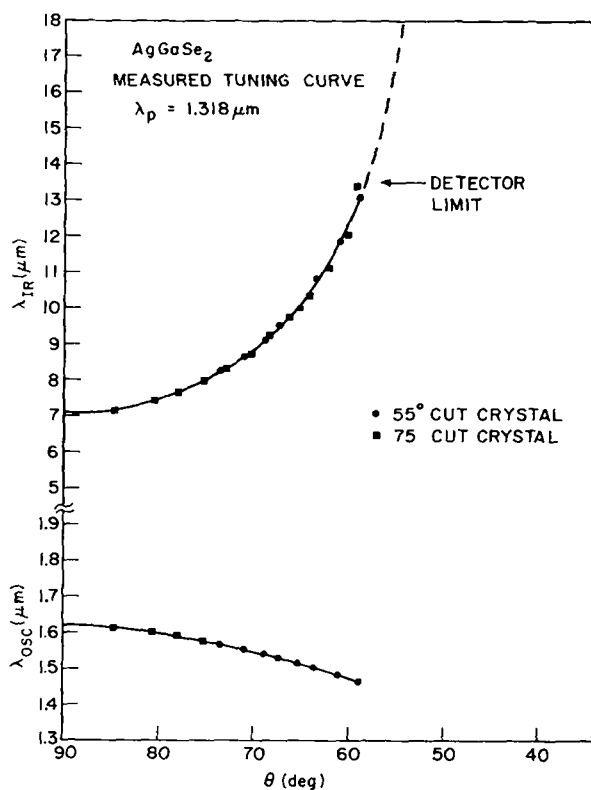

FIG. 2. — Tunable infrared (ω_1) down-conversion in AgGaSe₂ from a fixed frequency (ω_3) Nd : YAG laser and a LiNbO₃ parametric oscillator (ω_2) from BYER et al., Applied Physics Letters 24 (1974) 65.

A step-tuned sub-millimetre down-converter based upon ZnGeP₂ and CO₂ lasers [25] demonstrated some of the possibilities offered by ternary compounds in this region of the spectrum. There is fairly direct competition however from cubic semiconductor crystals such as GaAs [77, 78] ; phase-matching to the sub-millimetre is possible with cubic crystals through the long-wave dispersion from the restrahl bands.

4.2 ELECTRO-OPTIC MODULATORS. — With appropriate arrangements of applied field, light polarisation, etc., the electro-optic effect can be used to achieve either amplitude or phase modulation (see Fig. 3). The voltage which must be applied to the crystal electrodes for 100 % modulation is

$$V_{\lambda/2} = \frac{\lambda^3}{n^3 r_c} \cdot \frac{d}{l},$$

where $r_c = r_{41}$ for E(0) along x_1 or x_2,
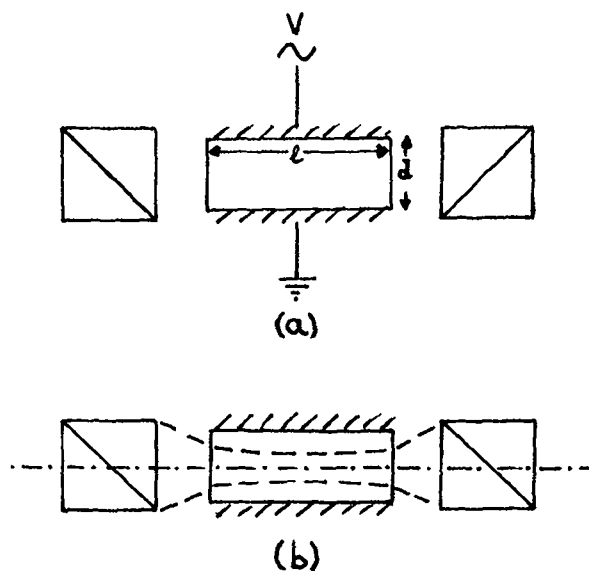
$\quad\quad = r_{63}$ for E(0) along x_3.

FIG. 3. — Electro-optic modulators ; (a) amplitude modulator, (b) phase modulator.

More important in practice is the power which must be supplied to the capacitor formed by the crystal and electrodes. The latter consideration leads to a figure-of-merit for electro-optic crystals

$$F = \frac{r_c^2 n^7}{\varepsilon_r(0)},$$

where $\varepsilon_r(0)$ is the crystal dielectric constant seen by the driving field. Refraction at the entrance and exit faces of the crystal leads to an extra factor of n in the numerator.

ZnGeP₂ has the largest figure-of-merit of the ternary compounds studied to date and this is very close to the value for GaAs (see Table III). There are however particular advantages with GaAs ; it is a cubic crystal so there is no need to compensate for natural birefringence, and it can already be grown to useful sizes and of high resistivity.

5. Lasers. — Direct gaps and relatively narrow luminescence bands (at least at low temperatures) are favourable conditions for obtaining stimulated emission/laser action in the ternary compounds. An excitation mechanism is required to induce the *population inversion* required by the Bernard-Durrafourg condition [79] ;

$$F_c - F_v > h\nu \, ,$$

where F_c and F_v are quasi-Fermi levels for conduction and valence bands respectively and ν is the frequency of the radiation emitted.

Stimulated emission has been achieved in six ternary compounds (Table IV) through *brute force* pumping with, either a high voltage electron beam and consequent avalanche excitation, or optically by use of a pulsed high power laser of photon energy greater than the band-gap. Threshold power densities range from

TABLE IV

Laser action

Ternary	T, K	Excitation	Operation	λ, μm
CdSiAs$_2$	80	20 kV electrons	S-F	0.766
CdSnP$_2$	80	25 kV electrons	Modes	1.011
CdSnP$_2$: Ag	80	0.38 μm laser	Modes	1.016
CuGaS$_2$	2	—	S-F	0.500
CuInS$_2$	2	—	S-F	0.818
AgGaS$_2$	2	—	S-F	0.462
AgGaSe$_2$	2	—	S-F	0.698

S-F : super-fluorescence.

10 to 50 kW/cm^2 for electron beam pumping [80, 81] and from 50 to 750 kW/cm^2 for laser pumping [82-84]. Laser action was confirmed by a narrowing of the luminescence bandwidth and by some beam directionality for those compounds which only exhibited super-fluorescence — that is amplified spontaneous emission, and for CdSnP$_2$ [80, 82, 83] by observation of modes of the Perot-Fabry resonator formed by the polished or cleaved faces of the crystal.

The above experiments should be viewed as having demonstrated the potentiality of ternary compounds for lasers rather than indicating any devices. A practical semiconductor laser will use direct carrier injection at a junction — a diode laser.

6. Junction devices. — The present interest in ternary semiconductor junction devices is for electroluminescence — LED's and possibly diode lasers — and for photodetectors. Both homojunction and heterojunction diodes have their own distinct advantages and disadvantages.

6.1 HOMODIODES. — As indicated in Section 2 a limited number of ternary compounds can be produced with both p- and n-type conduction, and low resistivity. Crude homojunctions were made in CdSnP$_2$ [14], CuInS$_2$ [84] and CuInSe$_2$ [85] by dopant

diffusion or by stoichiometry variation with a vapour anneal. The latter technique was used with CuInSe$_2$ to yield the first genuinely characterisable ternary homodiode [86]. n-type CuInSe$_2$ was subjected to a short anneal in Se vapour to produce a junction a short distance below the crystal surface ; the crystal was then etched to a mesa structure. A rectification ratio of 300 : 1 was attained for $\pm$ 1 V. With a forward bias, electroluminescence was obtained centred on 1.34 μm and with 10 % *internal* quantum efficiency at 77 K. Very recently [87], high quality homojunctions have been fabricated in CuInS$_2$. These diodes have rectification ratios in excess of 10 000 : 1 and also exhibit some electroluminescence.

6.2 HETERODIODES. — Diodes formed from two different semiconductor materials offer particular advantages in photodetection. Thus a large difference in band-gap between the two materials allows the radiation to enter through the large gap material and the resulting photodetector has a sensitive *window* for photons of energy falling anywhere between the two gaps. A direct transition for the lowest gap material ensures that the photocarriers are produced no more than a few microns from the depletion layer.

A basic requirement for the fabrication of a heterojunction is that the lattices of the two materials match each other ; for instance a binary compound with the sphalerite structure can be grown epitaxially on the (001) plane of a ternary crystal provided the a lattice parameters are comparable. The first reported ternary heterodiode [88] used n-type CdSnP$_2$ coupled with the cubic form of Cu$_2$S which was p-type. The lattice mismatch in this case was $\sim$ 5 % but a large photovoltaic response was still obtained with white light illumination.

A much better lattice match is possible with CdSnP$_2$: InP and heterodiodes have been made which exhibit both a photovoltaic response, as well as electroluminescence when forward biased [89, 90]. The photovoltaic quantum efficiency of a CdSnP$_2$: InP heterodiode is depicted in figure 4 where the spectral response is seen to extend from the 1.35 eV band-gap of InP to the 1.15 eV gap of CdSnP$_2$. The maximum quantum efficiency is $\sim$ 13 % and there is a useful response for wavelengths beyond the limit of Si diodes. The most promising heterodiode appears to be that based on CuInSe$_2$: CdS [91]. This heterodiode has essentially unity quantum efficiency from 0.55 to 1.25 μm and may therefore find application as a solar cell. In addition, specially prepared CuInSe$_2$: CdS photodiodes have a response time as short as $\sim$ 5 nanoseconds. Useful electroluminescence can also be obtained.

Green electroluminescence has been achieved (Fig. 5) with CuGaS$_2$: CdS heterodiodes [92, 93]. The *external* quantum efficiency of $\sim$ 0.1 % at 77 K must however be compared with the value of greater than 0.5 % obtained at *room temperature* for green emitting GaP : N LED's. It must of course be appreciated that
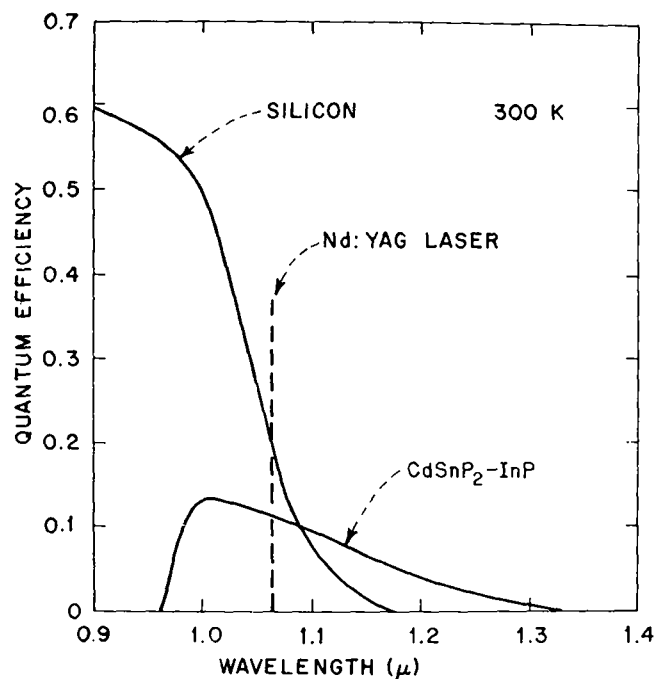
Fig. 4. — Wavelength dependence of photovoltaic quantum efficiency for a CdSnP₂ : InP heterodiode (shown for comparison is the quantum efficiency of a commercial Si detector) from Shay et al., *Applied Physics Letters* 23 (1973) 226.

Fig. 5. — Electroluminescence spectrum of a $CuGaS_2$: CdS heterodiode (The arrows indicate the positions of the $CuGaS_2$ band-gap at 77 and 291 K) from Wagner et al., *Applied Physics Letters* 22 (1973) 351.

diodes based upon elementary or binary semiconductors have achieved a high state of development. There remains a search for an efficient blue emitting LED and $CuAlS_2$ is a possible candidate for this application.

7. Other devices. — Device research outside the opto-electronic areas outlined above has been rather limited. Early on there was substantial interest in possible application of ternary compounds in thermoelectric devices [94, 95] but this has been overtaken by developments in alloy semiconductor materials with much more suitable properties.

Acousto-electric effects have been discovered offering the prospect of Gunn-type devices. Most work has been on $CdSnP_2$ with the characteristic threshold field and current saturation being observed [96] as well as coherent oscillation for one sample [97] at ~ 500 MHz. Considerably more research is needed to elucidate these phenomena before any potential device is considered.
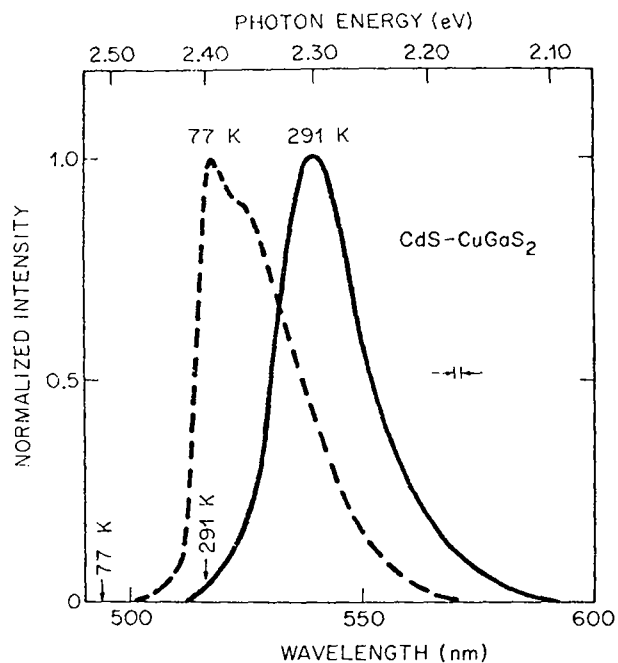
8. Conclusions. — Hopefully this review has demonstrated growing activity and confidence in the device applications of the ternary semiconductor compounds. It is worth noting that virtually all the significant developments have occurred within the past five years. It may be that as the 1950's saw the emergence of practical semiconductor devices based on the elements Ge and Si and the 1960's viable binary compound devices, in the present decade ternary devices will become established. The history of GaAs is worth recalling as it indicates that device applications can end up very different from those first conceived ; GaAs was initially studied as an alternative material for transistors with high thermal stability, it was then used in LED's and diode lasers, and finally Gunn effect devices emerged really without warning. There is no doubt that any successes with ternary devices will result only from a combination of improved quality and better characterised crystals and from systematic and imaginative device research.

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