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GLANCES AT TERNARY COMPOUNDS

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Abstract. — In the large family of ternary compounds one could expect to find systematic trends in the growth of our knowledge of these materials. I will then discuss several points related with the structural properties of ternary compounds and their chemical bonds. I will show that very simple questions have not yet received satisfactory answers and emphasize some problems which remain unsolved.

Introduction. — In this opening talk of the Second International Conference on Ternary Semiconducting Compounds I would like first to recall some historical steps in the growth of our knowledge of these materials. I will then discuss several points related with the structural properties of ternary compounds and their chemical bonds. I will show that very simple questions have not yet received satisfactory answers and emphasize some problems which remain unsolved.

1. Brief historical recall [1, 2]. — Elementary crystals and binary compounds exhibiting semiconducting properties have been known long time ago. The invention of the transistor in the late forties boosted the era of semiconductors and stimulated the search for new semiconducting materials. In 1962 the discovery of laser action in semiconductors gave a new incentive to the investigation of new materials.

In the early fifties it was shown by Hahn et al. [3] and by Goodman et al. [4] that the \(245_2\) compounds were a natural extension of the 35's and that the \(136_2\) compounds were a natural extension of the 26's. Although minerals belonging to these classes of ternary compounds were known a systematic investigation in fact started only after this pioneering work. This was a part of a systematic analysis of tetrahedral structures, primarily carried out by Parthe [1].

The Leningrad group under the late Goryunova [5] made significant contribution to this field. This group was the first to observe optical nonlinear properties [6] and to demonstrate laser action in a ternary compound [7]. More recently Chemla, Kupecek, Robertson and Smith [8] demonstrated phase-matched second harmonic generation in a chalcopyrite crystal. In the last five years several groups have been very active in various countries mainly on linear and nonlinear optical properties, on semiconducting properties and luminescence. Laser action has been studied in several ternary compounds by Bell Telephone Laboratories' scientists. Shay and coworkers [2] have shown that the quasi-cubic model of band structure is very adequate to derive band structure of \(245_2\) from the band structure of 35's. They also showed that a somewhat similar situation hold for the 136, which can be derived from the 26, if provision is made for the additional perturbation due to the d-band of the monovalent atom (Cu or Ag).

2. Valence and structure. — Most of the ternary compounds have tetrahedral structures. Fourfold coordinated compounds (binary, ternary quaternary, etc.) have a remarkable position among anorganic crystals. Parthe [1] has shown that there are precise relationship between the electronic valence of the atoms and the structure.

In a tetrahedral structure each atom has four nearest neighbours which form a more or less regular tetrahedron. Two nearest neighbours are bonded by the overlap of two valence electrons' wave functions. This overlapping of sp3 hybrids accounts for the cohesive energy just like in purely covalent crystals, like diamond, silicon and germanium. Besides these normal tetrahedral structures one can consider the bond defect tetrahedral structures in which some atomic sites are
empty. Around such a vacant site there are electron lone pairs.

Let \( \text{VEC} \) be the valence electron concentration, i.e. the average number of electrons per atom, and let \( x \) be the relative number of vacant sites. It was shown by Parthe [1] that:

\[
\text{VEC} = 4 + x.
\]

On the other hand let \( N_e \) be the number of valence electrons per unit formula and \( N_A \) be the number of anions.

Many of the tetrahedral compounds belong to the class of adamantine structures. An adamantine structure is a three dimensional tetrahedral structure for which \( N_e/N_A = 8 \). This include the normal tetrahedral structures and the bond defect tetrahedral structures described above. In adamantines there are no anion-anion bond and no cation-cation bond.

The above rules are of great help in indicating the composition of possible tetrahedral structures. These necessary conditions are obviously insufficient to ascertain that the actual structures are fourfold coordinated.

3. Crystallographic structure of chalcopyrite. — As mentioned above most of the ternary compounds are adamantines, tetrahedrally coordinated. Among these many of them have the so-called chalcopyrite structure. Let us recall it briefly.

Let us replace one Zn atom out of two by a cation of lower valence, Cu for instance, and the other one by a cation of higher valence, Fe for instance (Fig. 2). At this point we can make a few remarks:

1) The average number of valence electrons provided by cations is unchanged and this makes possible for the new structure, the chalcopyrite, to retain the tetrahedral arrangement of the original zincblende.

2) From the 35 compounds and the 26 compounds we can derive two families of ternary compounds, respectively the 245,'s and the 136,'s.

3) It can be shown that if the replacement of Zn atoms by Cu and Fe on the cationic sublattice is made in a regular way, compatible with translation invariance, as it ought to be in a true crystal, then the Bravais lattice unit cell has to be doubled. For instance there must be two cubic cells along the \( z \) axis to form the quadratic unit cell of the chalcopyrite. However the primitive unit cell of the chalcopyrite contains 8 atoms \( (\text{Cu}_2\text{Fe}_2\text{S}_4) \) and is four times larger than the corresponding primitive unit cell of the zincblende which contains only two atoms (S and Zn). As a result the first Brillouin zone of the chalcopyrite is four times smaller than the first Brillouin zone of the zincblende.
4) If the cations are randomly distributed on the cationic sublattice, as this is the case for several ternary compounds, then the structure is that of zincblende by cationic disorder.

5) In the zincblende structure each S atom is at the center of a tetrahedron with four Zn atoms at each corner. The four bonds have all the same length and are symmetrically equivalent in space making a very well known angle of 109°45. When two Zn atoms are replaced by Cu and the two other Zn atoms are replaced by Fe the four bonds are no longer identical: the distance between S and Cu is not exactly equal to the distance between S and Fe. In other words the tetrahedron is no longer regular but is slightly deformed along the two-fold axis. However this distortion in most compounds is not very large and the orbitals remain very close to $sp_3$ hybrids.

![Fig. 3. Tetrahedron distortion in chalcopyrite.](image)

To summarize we can say that the lattice period $c$ is not exactly equal to $2a$ (Fig. 3). This is characterized by a dimensionless parameter:

$$\tau = 2 - \frac{c}{a}$$

which takes into account the dilatation or the compression along the z-axis.

On the other hand the displacement of the S atoms due to bonds’ length difference is alternatively along the +z and the $-x$ axis and along the $+y$ and $-y$ axis. If $x$ is the actual position of the S atom in the cell this displacement is measured by the dimension less parameter

$$\sigma = \left| \frac{4x}{a} - 1 \right| .$$

The point group of the zincblende is $43m$. In the chalcopyrite the 3-fold axis is lost, the symmetry class is now $42m$. The space group of the chalcopyrite is $I42d$ (or $D_{4h}^{12}$). Only the knowledge of the structure of each ternary chalcopyrite crystal can provide us with the actual values of the parameters $\tau$ and $\sigma$. Conversely if $\tau$ and $\sigma$ were known from, say a theoretical model, then the actual positions of the atoms would be known. The crystallographic structures have been determined for several chalcopyrites but are unknown for many ternary compounds (chalcopyrites included).

Many of the physical properties of the chalcopyrite crystals depend to some extent on the values of $\tau$ and $\sigma$. On the other hand can we predict the actual values of $\tau$ and $\sigma$ from the atomic parameters of the constituents of a ternary compound? Or in other words do we have a physical model that can explain which values they take for a given crystal? In the case of 245$_2$ compounds Abrahams and Bernstein [9] have shown that the tetrahedra surrounding the atoms of valence four are regular and this results in the relationship

$$\tau = \sigma .$$

In a paper of this session Chemla, Deschanvres and Mercey [10] show that the actual value of the tetragonal compression $\tau$ can be quantitatively explained by taking into account the covalent radii of the atoms and the electronegativity differences of the 25 and the 45 bonds. This may result in a better understanding of several properties strongly dependent on structure, such as birefringence, nonlinear susceptibilities, photoelasticity, etc...

Moreover it appears that two of the 245$_2$ compounds, ZnSnAs$_2$ and ZnSnP$_2$, which do not fit this model have probably a structure slightly different from an exact chalcopyrite structure as shown in a paper of this session by Y. Montfort, J. Vizot and G. Allais [11]. It should be noticed that these two compounds have almost no tetragonal compression ($\tau \approx 0$).

In the case of the 136$_2$ compounds, where we have no evidence that some tetrahedra are regular the situation is not so simple and we have not yet an approach of the problem.

**4. Alloys, disorder and amorphism.** Many solid solutions are known. For instance solid solubility has been observed in several adamantine compounds as shown in table I.

We have already mentioned that in many 245$_2$ compounds cations may occupy random positions on the cationic sublattice. This results in a disordered zincblende structure. The chalcopyrite phase is stable at low temperature and the zincblende disordered structure, stable at high temperature, is often retained at room temperature by fast cooling. Usually the transition temperature is $50^\circ C$ to $100^\circ C$ below the melting temperature. Is the existence of such a high temperature phase correlated with some structural parameter like the compression $\tau$ or with some chemical property like ionicity? Correlations of this kind have not yet been reported, perhaps because precise experimental data are still too scarce.

In the case of the 136$_2$ compounds it seems that this zincblende structure by cationic disorder is much less frequent than in the 245$_2$ compounds. Again more experimental data is required.
On the other hand a few ternary compounds are known to display amorphous state: how is this linked with chemical binding or with the structural parameters of the corresponding crystalline form?

5. Chemical bond and coordination number. — As we know many ternary compounds are not of the chalcopyrite structure. We have just seen that there are now two examples where the actual structure is slightly different from the chalcopyrite. But many tetrahedral ternary compounds have a structure very different from chalcopyrite. More precisely they often display a particular structure which is derived from wurtzite much in the same way chalcopyrite is derived from sphalerite. Moreover several ternary compounds are not tetrahedrally coordinated but have a six-fold or an eight-fold coordination.

Let us come back for a moment to binary compounds of the $A^N B^8 - N$ type where approximately 70 crystals are known.

J. C. Phillips [12] describes bonding energy by an average energy gap or dielectric gap $E_G$ which is given by:

$$ E_G = E_h^2 + C^2 $$

where $E_h$ is the covalent contribution and $C$ is the ionic contribution. He defines the ionicity of a bond by the ratio:

$$ f = \frac{C^2}{E_G} $$

It was shown by J. C. Phillips that a remarkable trend appears when one represent each binary compound on a $(C, E_h)$ chart (Fig. 4). It turns out that zincblende, wurtzite and rocksalt structures correspond to different regions of the $(C, E_h)$ plane. In particular rocksalt crystals, six-fold coordinated, appear only in the region where:

$$ f \geq 0.785. $$

In the other part of the plane the four-fold coordinated crystals, wurtzite and zincblende structures, are separate by a curve but not in the same rigourous manner.

This empirical behaviour can be understood by the following qualitative argument. With increasing ionicity the valence electrons are closer to the anion, the overlap between $sp_3$ hybridized wavefunctions decreases and the binding energy is lower. For too high an ionicity the tetrahedral structure is no longer stable because the atomic arrangement can gain cohesive energy by switching to an octahedral structure six-fold coordinated. This has been quantitatively studied by Walter and Cohen [13]. However the role of pressure, temperature, impurities, alloying, etc... require more experimental data and would probably stimulate more refined theoretical analysis.

Now we may ask ourselves if the ionicity is related with the coordination of the actual structures of the ternary compounds as it is for the binary compounds?

Consider a ternary compound $ABC$ and assume it is
tetrahedral. We can apply the Phillips concepts of dielectric gap $E_G$ and ionicity $f$ for each bond AC and BC, with:

$$f_{AC} = \frac{C_{AC}^2}{E_G^2(AC)} \quad f_{BC} = \frac{C_{BC}^2}{E_G^2(BC)}.$$

### Table II

<table>
<thead>
<tr>
<th>ABC$_2$ compound</th>
<th>$f_{AC}$</th>
<th>$f_{BC}$</th>
<th>Structure</th>
<th>Coordination</th>
</tr>
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<td>ZnSiP$_2$</td>
<td>0.53</td>
<td>0.13</td>
<td>Ch</td>
<td>4</td>
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<tr>
<td>ZnSnP$_2$</td>
<td>0.54</td>
<td>0.17</td>
<td>Ch</td>
<td>4</td>
</tr>
<tr>
<td>ZnSiAs$_2$</td>
<td>0.49</td>
<td>0.66</td>
<td>Ch</td>
<td>4</td>
</tr>
<tr>
<td>ZnGeAs$_2$</td>
<td>0.50</td>
<td>0.18</td>
<td>Ch</td>
<td>4</td>
</tr>
<tr>
<td>ZnSnAs$_2$</td>
<td>0.52</td>
<td>0.29</td>
<td>Ch</td>
<td>4</td>
</tr>
<tr>
<td>CdSiP$_2$</td>
<td>0.58</td>
<td>0.14</td>
<td>Ch</td>
<td>4</td>
</tr>
<tr>
<td>CdGeP$_2$</td>
<td>0.59</td>
<td>0.18</td>
<td>Ch</td>
<td>4</td>
</tr>
<tr>
<td>CdSnP$_2$</td>
<td>0.62</td>
<td>0.31</td>
<td>Ch</td>
<td>4</td>
</tr>
<tr>
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<td>0.7</td>
<td>Ch</td>
<td>4</td>
</tr>
<tr>
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<td>0.1</td>
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<tr>
<td>CdSnAs$_2$</td>
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<td>0.23</td>
<td>Ch</td>
<td>4</td>
</tr>
<tr>
<td>AgAlS$_2$</td>
<td>0.7</td>
<td>0.56</td>
<td>Ch</td>
<td>4</td>
</tr>
<tr>
<td>AgGaS$_2$</td>
<td>0.7</td>
<td>0.54</td>
<td>Ch</td>
<td>4</td>
</tr>
<tr>
<td>AgInS$_2$</td>
<td>0.72</td>
<td>0.64</td>
<td>Ch</td>
<td>4</td>
</tr>
<tr>
<td>AgAlSe$_2$</td>
<td>0.67</td>
<td>0.51</td>
<td>Ch</td>
<td>4</td>
</tr>
<tr>
<td>AgGaSe$_2$</td>
<td>0.68</td>
<td>0.51</td>
<td>Ch</td>
<td>4</td>
</tr>
<tr>
<td>AgInSe$_2$</td>
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<td>0.69</td>
<td>Ch</td>
<td>4</td>
</tr>
<tr>
<td>AgAlTe$_2$</td>
<td>0.62</td>
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<td>Ch</td>
<td>4</td>
</tr>
<tr>
<td>AgGaTe$_2$</td>
<td>0.62</td>
<td>0.41</td>
<td>Ch</td>
<td>4</td>
</tr>
<tr>
<td>AgInTe$_2$</td>
<td>0.64</td>
<td>0.51</td>
<td>Ch</td>
<td>4</td>
</tr>
<tr>
<td>CuAlS$_2$</td>
<td>0.5</td>
<td>0.54</td>
<td>Ch</td>
<td>4</td>
</tr>
<tr>
<td>CuGaS$_2$</td>
<td>0.65</td>
<td>0.54</td>
<td>Ch</td>
<td>4</td>
</tr>
<tr>
<td>CuInS$_2$</td>
<td>0.68</td>
<td>0.64</td>
<td>Ch</td>
<td>4</td>
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<tr>
<td>CuAlSe$_2$</td>
<td>0.63</td>
<td>0.57</td>
<td>Ch</td>
<td>4</td>
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<tr>
<td>CuGaSe$_2$</td>
<td>0.63</td>
<td>0.49</td>
<td>Ch</td>
<td>4</td>
</tr>
<tr>
<td>CuInSe$_2$</td>
<td>0.65</td>
<td>0.57</td>
<td>Ch</td>
<td>4</td>
</tr>
<tr>
<td>CuAlTe$_2$</td>
<td>0.56</td>
<td>0.38</td>
<td>Ch</td>
<td>4</td>
</tr>
<tr>
<td>CuGaTe$_2$</td>
<td>0.57</td>
<td>0.39</td>
<td>Ch</td>
<td>4</td>
</tr>
<tr>
<td>CuInTe$_2$</td>
<td>0.59</td>
<td>0.48</td>
<td>Ch</td>
<td>4</td>
</tr>
<tr>
<td>CaCN$_2$</td>
<td>0.77</td>
<td>0.2</td>
<td>I</td>
<td>&gt;6</td>
</tr>
<tr>
<td>LiAlO$_2$</td>
<td>0.82</td>
<td>0.74</td>
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<td>&gt;6</td>
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<tr>
<td>NaInO$_2$</td>
<td>0.87</td>
<td>0.72</td>
<td>I</td>
<td>&gt;6</td>
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<tr>
<td>NaInS$_2$</td>
<td>0.76</td>
<td>0.61</td>
<td>I</td>
<td>&gt;6</td>
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<tr>
<td>NaInSe$_2$</td>
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<td>0.57</td>
<td>I</td>
<td>&gt;6</td>
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<tr>
<td>LiInO$_2$</td>
<td>0.86</td>
<td>0.85</td>
<td>I</td>
<td>&gt;6</td>
</tr>
<tr>
<td>KO$_2$</td>
<td>0.88</td>
<td>0.70</td>
<td>I</td>
<td>&gt;6</td>
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<tr>
<td>NaBO$_2$</td>
<td>0.86</td>
<td>0.66</td>
<td>I</td>
<td>&gt;6</td>
</tr>
<tr>
<td>β-LiGaO$_2$</td>
<td>0.86</td>
<td>0.78</td>
<td>W</td>
<td>4</td>
</tr>
<tr>
<td>LiGaS$_2$</td>
<td>0.76</td>
<td>0.55</td>
<td>W</td>
<td>4</td>
</tr>
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<td>LiInS$_2$</td>
<td>0.78</td>
<td>0.63</td>
<td>W</td>
<td>4</td>
</tr>
<tr>
<td>NaGaO$_2$</td>
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<td>0.80</td>
<td>W</td>
<td>4</td>
</tr>
<tr>
<td>BeSiN$_2$</td>
<td>0.61</td>
<td>0.47</td>
<td>W</td>
<td>4</td>
</tr>
</tbody>
</table>

Ch = Chalcopyrite.  
I = Ionic.  
W = Wurtzite.

For each known compound we can calculate its two bond ionicities (see Table II) and on a $(f_{AC}, f_{BC})$ chart we can indicate if the actual structure is tetrahedral (4-fold coordinated) or octahedral (6-fold or 8-fold coordinated). This is shown on figure 5. It is clear that if one of the two bond ionicities is larger than 0.75-0.78 then the tetrahedral structure is replaced by an octahedral one, having a coordination number equal to six or more.

6. The « anionic » ternary compounds. — Coming back to the derivation of the ternary compounds from the 35's and from the 26's we must notice that we have only considered the splitting of the cation lattice. 245$_2$ compounds are derived from 35 by replacing two atoms of the third column by one of the second and one of the fourth. 136$_2$ compounds are derived from 26's by replacing two atoms of the second column by one atom of the first column and one of the third. We shall call these ternaries of the « cationic type » b-cause it is generated by cationic substitution. Incidentally among all the possible 245$_2$ compounds and 136$_2$ compounds several are not known. Have they not been observed or could they not be prepared?

By a symmetry argument one would expect two other families, namely the 3,46 and the 2,57, derived by substitution in the anion lattice (Fig. 6). As a matter

![Figure 5](image_url)

**Fig. 5.** — Ionicities of several ternary compounds.

- Tetrahedral derived from sphalerite.
- Tetrahedral derived from wurtzite.
- Coordination number higher than 4.

![Figure 6](image_url)

**Fig. 6.** — Derivation of ternary compounds from 35 and 26 binary compounds.
of fact only two of these anionic ternary compounds have been clearly identified: \( \text{Al}_2\text{CO} \), a \( \text{Si}_2\text{46} \) compound known for many years, and \( \text{Zn}_2\text{NF} \), a \( \text{Si}_2\text{57} \) discovered by Marchand and Lang [14] a few years ago.

This fact is rather surprising and has not yet received any explanation. Apparently these compounds are not frequent as natural minerals but does this means that they cannot be prepared in laboratory? Did we lack of imagination to think of these possible materials or do we lack of faith to start growing them? Because it is not very frequent to publish unsuccessful attempts one may also conjecture that several groups have tried and failed. It would be interesting enough to disclose these attempts. On the other hand chemists and physicists may have some good theoretical arguments explaining why these materials can hardly exist. I suggest that these problems could be the matter of an informal discussion during the Conference.

7. Defect compounds. — Some binary compounds, like for instance \( \text{Ga}_2\text{S}_3 \), are adequately described as defect ternary compounds. \( \beta\text{-Ga}_2\text{S}_3 \) is very close to wurtzite: \( \text{S} \) atoms occupy all the \( \text{S} \)-sites while \( \text{Ga} \) occupy only 2 \( \text{Ga} \)-sites out of 3; one \( \text{Ga} \)-site out of 3 remains vacant. For another temperature range appears the \( \gamma \)-form of \( \text{Ga}_2\text{S}_3 \), similar to zincblende, with again \( \frac{1}{3} \) of the \( \text{Zn} \)-sites occupied by \( \text{Ga} \). In both \( \beta \) and \( \gamma \) forms, \( \text{Ga} \) vacancies are randomly distributed. In a third form, \( \alpha\text{-Ga}_2\text{S}_3 \), a superstructure based upon wurtzite, the \( \text{Ga} \) vacancies are ordered. All attempts to fill \( \text{Ga} \) vacancies of \( \text{Ga}_2\text{S}_3 \) with \( \text{Ga} \) atoms fail and one ends with a mixture of \( \text{Ga}_2\text{S}_3 \) and \( \text{GaS} \). One can say that \( \text{Ga}_3\text{S}_3 \) is a ternary compound of the form \( \text{O}_3\text{S}_6 \) where \( \text{O} \) is a fictitious atom of valence 0. Such a compound can be derived, as shown several years ago by Suchet [15] from the Grimm-Sommerfeld rule. \( \text{Ga}_2\text{S}_3 \) belongs to the general family of defect structures. It can be noticed that defect compounds always involve the vacancy of a cationic site and never of an anionic site.

Around a vacant site it is believed that there are lone pairs or dangling bonds. Almost nothing is known on these electron pairs. How much do they take part in the cohesive energy? What are their spatial orientation? Which role do they play in dielectric properties, linear or nonlinear?

On the other hand these defect structures can be considered as clathrates with very small cages. An this brings a question which, apparently, has not been payed any attention. We know real atoms which have valence 0 and they are the rare gas atoms of the 8th column. As far as I know ternary compounds containing rare gas atoms have not been reported. It would be interesting to know if \( 3\text{Z}_{2}\text{8} \) compounds like \( \text{Ga}_3\text{S}_3\text{Ne}, \text{Ga}_3\text{S}_3\text{Ar}, \text{Ga}_3\text{S}_3\text{Kr} \) can be prepared. This may bring some light to the question of the lone pairs and contribute to understand the binding of rare gases.

Conclusion. — Let us have a look at figure 7 where I have plotted the number of publications on ternary compounds per year as a function of time. Obviously the boom on these compounds is quite recent and started really in 1966. During the last eight years a very large amount of information has been obtained. The rate at which experimental data and physical understanding has been gathered is considerably larger than it would have been twenty, or even ten years ago. This is the result of several factors:

- Material Science has wider possibilities.
- Experimental methods are much more efficient.
- Better theoretical tools are available and more widely spread.
- Ternary compounds are close to the large class of binary compounds: apparently the ternaries can be understood as an extension of the binaries without the requirement of important new concepts.

However we must be aware that, in the future, for new classes of materials, the situation might be different and new tools could be required.

The curve shown in figure 7 indicate that in 1972 there is a decrease in the number of publications on ternary compounds. Data concerning 1973, although they are not ascertained, confirm this tendency. This is evidence that the progress in understanding ternary compounds is continuing but at a slower rate.

The initial unformal anglo-french meeting in Bagneux (Nov. 1972), then the First International Conference in Bath (Nov. 1973) have certainly been useful in collecting informations, in getting together people involved in similar problems, in promoting studies on ternary compounds. The Second International Conference which is just starting today will also have, I am sure, a positive impact. However
during this conference we must certainly think about the future of ternary compounds.

Having asked several questions in my talk I would like to conclude with a final one: do we have good enough arguments to consider ternary compounds as having specific characteristics or are we inclined to consider these materials just like semiconductors, among many others?

Acknowledgments. — This review has benefited from Daniel Paquet’s contribution who carried out the calculation of bond ionicities for several ternary compounds.

It is a pleasure to acknowledge several fruitful discussions with D. Chemla and J. Jerphagnon.

I would like to thank Dr. Shay whose book was available for me before publication.

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[1] PAKTHE, E., Cristallochimie des structures tétraédriques (Gordon and Breach) 1972. This book contains a very large bibliography.