parameters of the tetragonal structure are not a unique function of temperature, *i.e.* they depend on the direction of transformation. On the other hand, all parameters of the m phase having a normal linear temperature dependence in its range of existence are practically identical to those that occur during the $m \rightarrow t$ transformation at the same temperatures.

From extrapolating the B factors down to 0 K we deduce some static disorder is present in the m phase. The same procedure for the t modification gives no indication of such behaviour. On the other hand, the presence of a modulated diffuse background (in the stability range of the t phase) means that there is some kind of disorder which might therefore be of dynamic origin. We have no direct evidence for this, however, and clearly more experiments, in particular inelastic neutron experiments, are needed in order to clarify this point. There is evidence, however, that the tetragonal modification is intrinsically less 'rigid' than the monoclinic one. This is consequently important for the properties of ZrO_2-based materials.

In the paper (I) an orientational relationship $\mathbf{b}_t \| \mathbf{b}_m$ and $\mathbf{c}_t \| \mathbf{c}_m$ was suggested only for the precursor stage. Here we derived a different relationship, $\mathbf{c}_t \| \mathbf{b}_m$ and $\mathbf{a}_t \| \mathbf{a}_m^*$, from extrapolation of the lattice constants for the $t \rightarrow m$ transformation. Hence, it is not implausible that this relationship might also hold for the main part (second stage) of the $m \rightarrow t$ transformation. In fact, this conclusion could have been derived already from the earlier results [paper (I)]. It was not so clear, however, since only two points at the highest temperatures defined the linear temperature dependence in that experiment. Definite conclusions about orientational relationships are only possible by single-crystal experiments *via* inspection of the reciprocal lattices of coexisting m and t phases. Such an experiment has been carried out, but the results have not yet been evaluated (Mursic, Vogt, Frey & Boysen, 1991).

The similar behaviour of the microstrains in both cases favours the explanation given in paper (I), that they originate only from the specific microstructure of our sample and thus this probably rules out the other possibilities discussed in (I).

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A Master Diagram for the Quick Localization of Possible Homogeneity Ranges of Adamantane-Structure Compounds

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Abstract

The composition ranges of adamantane-structure compounds are controlled by two valence-electron equations. Based on these rules a master diagram can be constructed which allows the quick localization of possible homogeneity ranges of adamantane-structure compounds in any binary or ternary diagram. These theoretical predictions are compared with the reported experimental results on the homogeneity range of the adamantane structure in the system Cu–In–Se. The experimental data agree with the predictions; however, a deviation has been reported in one case. Possible explanations are given for this exception which needs to be verified in the future by a single-crystal structure study.

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Valence-electron rules for adamantane structures

Adamantane-structure compounds are normal-valence compounds where the cations and anions occupy the Zn and S sites, respectively, of the zinc-blende (sphalerite) or wurtzite structure (or another stacking variant). Zinc blende itself is an ordered substitution variant of diamond. The structural relationship to diamond (or a stacking variant of it) is the reason for the term 'adamantane structure'.

The compositions of the adamantane-structure compounds are governed by two valence-electron rules (Parthé, 1967, 1987, 1990) based on:

(*a*) the partial valence-electron concentration in respect to the anion, VEC_A, defined for a compound C_mA_n as:

$$VEC_A = (me_C + ne_A)/n \qquad (1)$$

(*b*) the total valence-electron concentration, VEC, defined as:

$$VEC = (me_C + ne_A)/(m + n) \qquad (2)$$

where e_C (e_A) is the number of valence electrons of the cation (anion) in the non-ionized state (which for the non-transition elements considered here corresponds to their group number in the periodic system).

Since the adamantane-structure compounds are normal-valence compounds one condition is that:

$$VEC_A = 8. \qquad (3)$$

Further, adamantane structures are tetrahedral structures and consequently the general tetrahedral stucture equation can be applied here:

$$VEC = 4 + N_{NBO} \qquad (4)$$

where N_{NBO} is the average number of non-binding orbitals per atom. The value of VEC can vary between 4 and 4·923, the upper limit, as discussed below, having been determined experimentally.

One distinguishes between:

(*a*) *normal adamantane structures* with composition C_nA_n, $VEC = 4$ and $VEC_A = 8$ where all Zn and S sites are fully occupied, and

(*b*) *defect adamantane structures* with composition $C_{n-p}\square_pA_n$, $VEC > 4$ and $VEC_A = 8$ where all S sites are occupied but some Zn sites are not (there are p sites unoccupied).

A vacancy $\square$ on a Zn site corresponds to four non-binding orbitals, one on each of the four tetrahedrally coordinated anion neighbours of the empty Zn site. Thus for $C_{n-p}\square_pA_n$:

$$N_{NBO} = (4p)/(n - p + n) = VEC - 4 \qquad (5)$$

and finally

$$p/n = 2 - 8/VEC \qquad (6)$$

which is known as the *adamantane-structure equation*.

The adamantane-structure equation correlates the number of Zn-site vacancies with the VEC value of the compound. This equation can also be used to calculate the average number of anion–cation bonds per anion, $NB_{A\to C}$, according to:

$$NB_{A\to C} = 4 - 4p/n = 4[(8/VEC) - 1]. \qquad (7)$$

Simple solutions of equations (6) and (7) together with known examples are given in Table 1. Note that some of the examples given correspond to compounds with an ordered arrangement of vacancies and cations on the Zn sites. Whether or not there are ordered structures does not depend on the valence-electron concentration and is beyond the scope of the discussion in this paper.

At the experimentally observed upper VEC limit of $4{\cdot}92_3$ three out of every eight cation sites are unoccupied and each anions has, on average, only 2·5 tetrahedral bonds to surrounding cations. This VEC limit results from studies by Radaoutsan (1964) on the solubility of $GeSe_2$ ($VEC = 5{\cdot}33_3$) in $Ga_2\square Se_3$ ($VEC = 4{\cdot}80$) which terminates at $(Ga_4Ge\square_3)Se_8$ ($VEC = 4{\cdot}92_3$). For compounds with larger VEC values more cations are missing and an anion participates, on average, in less than 2·5 anion–cation bonds, which means it has more than 1·5 lone-electron pairs attached to it. With more lone-electron pairs on the anion the angle between the remaining anion–cation bonds may show greater deviations from the ideal value of 109·4° due to a mutual repulsion of the lone pairs. Under these circumstances zinc-blende- and wurtzite-related structures do not form anymore. However, other defect tetrahedral structures can exist with higher VEC values, for example, SiO_2 with two O—Si bonds per O atom, where the Si—O—Si angle can vary from 144° for α-quartz to 80° for fibrous SiO_2.

Two comments should be made at this point. The given valence-electron rules are necessary, but not sufficient, conditions for the occurrence of an adamantane structure. Additional conditions, originally formulated by Mooser & Pearson (1959), have been

Table 1. *Simple solutions of the adamantane-structure equation together with examples*

VEC	4	$4{\cdot}26_7$	$4{\cdot}36_4$	$4{\cdot}57_1$	4·80	$4{\cdot}92_3$
p/n	0	1/8	1/6	1/4	1/3	3/8
$NB_{A\to C}$	4	3·5	$3{\cdot}33_3$	3	$2{\cdot}66_7$	2·5
Examples	ZnS	$Hg_5Ga_2\square Te_8$	$Hg_3In_2\square Te_6$	$CdGa_2\square S_4$	$Ga_2\square S_3$	$(Ga_4Ge\square_3)Se_8$

further developed by different authors (Phillips, 1981; Zunger, 1981; Villars, Mathis & Hulliger, 1989). Further, the presence of other very stable compound(s) in the system may lead to the non-appearance of an otherwise expected adamantane-structure compound, or to a homogeneity range which does not reach the *VEC* limit.

However, it can also be mentioned here that these valence-electron rules have been useful in the past for pinpointing errors in the composition of adamantane-structure compounds or for suggesting that the real structure is not a tetrahedral structure. For example, the compound Cu_2SnSe_4 ($VEC = 4{\cdot}28_6$, $VEC_A = 7{\cdot}5$) with disordered zinc-blende structure (Bok & de Wit, 1963) has, with great probability, the composition Cu_2SnSe_3 (Rivet, Laruelle, Flahaut & Fichet, 1970) or $Cu_2Sn_{1\cdot5}\square_{0\cdot5}Se_4$ ($VEC = 4{\cdot}26_7$, $VEC_A = 8$), if Cu_2SnSe_3 should really have a homogeneity range. Further, for the mineral binnite 'Cu_3AsS_3' with $VEC = 3{\cdot}71_4$ a tetrahedral structure had originally been proposed, but later it was found that the composition is $Cu_{12}As_4S_{13}$ and that one S atom is octahedrally coordinated (Wuensch, Takeuchi & Nowacki, 1966). Another example which can be mentioned is 'In_5S_4' with a tetrahedral structure, where the expected structural features did not agree with the observed ones. This problem has now been resolved since the correct composition is In_4SnS_4 (Parthé, 1990; Deiseroth, Kluge & Pfeifer, 1990).

A master diagram for finding possible homogeneity ranges

It is shown above that the compositions of the adamantane-structure compounds are controlled by the two equations: $VEC_A = 8$ and $4 \leq VEC \leq 4{\cdot}92_3$. A homogeneity range of ternary or multicomponent adamantane structures is thus, in principle, possible and involves a change of the *VEC* value within the given limits, with the VEC_A value remaining constant. In a ternary diagram the composition ranges of adamantane-structure compounds appear as lines. An adamantane structure is, however, not possible in every ternary diagram. It depends on the number of valence electrons of the component elements whether or not there are compositions possible for which $VEC_A = 8$ and where *VEC* lies within the given limits.

Fig. 1. shows a master diagram which allows the localization of possible homogeneity ranges of adamantane-structure compounds in any binary or ternary diagram. The numbers of valence electrons of the cations are given on the bottom line, those of the anions on the top line. By connecting appropriate points one obtains the triangle (in most cases non-equilateral) which corresponds to the ternary system, of interest. The compositions are coded, *i.e.* the elements have been indicated by numbers which correspond to their number of valence electrons. Adamantane-structure compounds can be found only on the short heavy line for which $VEC_A = 8$ and $4 \leq VEC \leq 4{\cdot}92_3$.

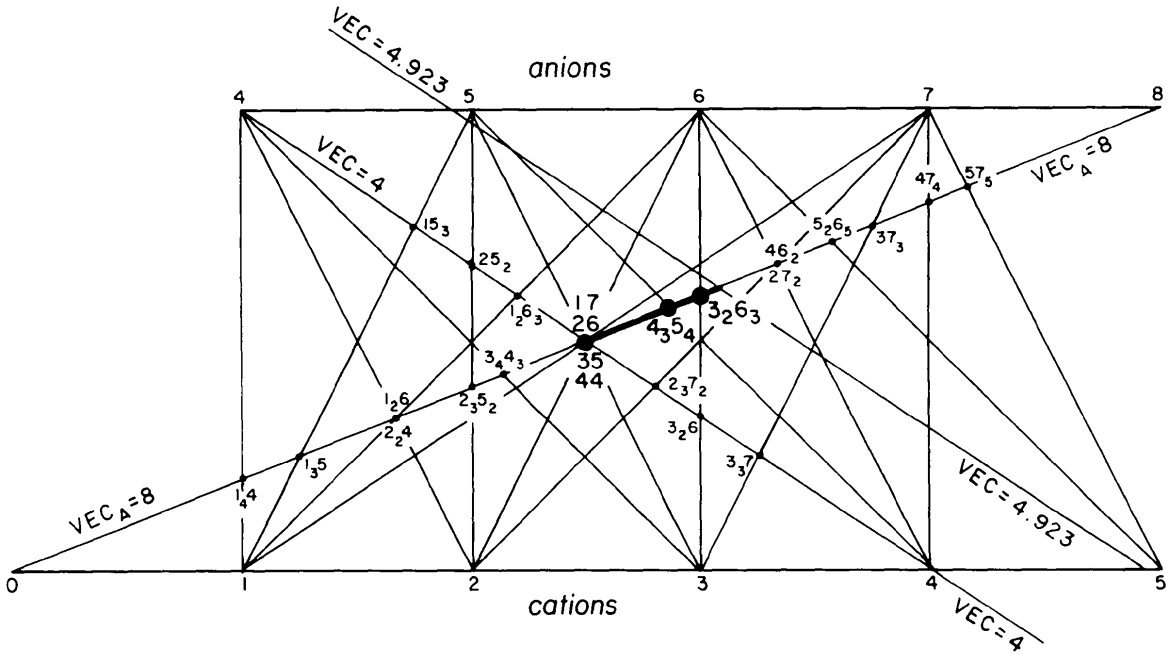

Fig. 1. A master diagram to find the possible homogeneity ranges of adamantane-structure compounds in any binary or ternary diagram. Adamantane structures are found only with compositions which are located on the thick line where $VEC_A = 8$ and $4 \leq VEC \leq 4{\cdot}92_3$. The compositions of possible binary adamantane-structure compounds are emphasized.

The following examples demonstrate the use of the master diagram:

System 1–3–5: Only a compound 35 could have an adamantane structure which has no homogeneity range.

System 1–4–6: The compound $1_2 46_3$ with a normal adamantane structure might have a homogeneity range which could reach up to $1_4 4_{11} \square_9 6_{24}$ ($VEC = 4{\cdot}92_3$). It is assumed that the element with four valence electrons behaves as a cation.

System 2–3–7: An adamantane structure is not possible.

System 3–4–6: The compound $3_2 \square 6_3$ ($VEC = 4{\cdot}80$) might have a homogeneity range which could reach up to $3_4 4 \square_3 6_8$ ($VEC = 4{\cdot}92_3$) (assuming that element 4 is a cation).

Pseudobinary system $1_2 6$–27_2: All compositions in this system correspond to normal-valence compounds. An adamantane structure is, however, possible only between $1_2 267_2$ ($VEC = 4$) and $1_4 2_{11} \square_9 6_2 7_{22}$ ($VEC = 4{\cdot}92_3$).

Pseudobinary system 35–$3_2 \square 6_3$: An adamantane structure is possible in the complete range.

Comparison of theoretical predictions and experimental results in the system Cu–In–Se

According to Fig. 1 the normal-valence compounds with $VEC_A = 8$ are to be found on the line between $1_2 6$ ('Cu_2Se') and $3_2 6_3$ (In_2Se_3). Adamantane structures can occur between 136_2, that is $CuInSe_2$ with $VEC = 4$, and $3_2 \square 6_3$, that is In_2Se_3 with $VEC = 4{\cdot}80$. The formula of the adamantane-structure compound for the complete range can be expressed either by:

$$Cu_{1-x}In_{1+(x/3)}\square_{2x/3}Se_2 \qquad (8a)$$

with $CuInSe_2$ corresponding to $x = 0$ and $In_{4/3}\square_{2/3}Se_2 \equiv In_2\square Se_3$ corresponding to $x = 1$, or by:

$$(1-y)Cu_2Se + yIn_2Se_3 \equiv Cu_{2-2y}In_{2y}\square_{2y-1}Se_{1+2y} \qquad (8b)$$

within the limits $y = 50\%$ ($CuInSe_2$) and $y = 100\%$ (In_2Se_3). The variables x and y are related as:

$$x = 3(2y-1)/(2y+1) \text{ and } y = \tfrac{1}{2}(3+x)/(3-x) \qquad (9)$$

provided that y is expressed as a fraction.

Data published by Palatnik, Komnik & Rogacova (1964), Konešova, Babycina & Kalinnikov (1982) and Boehnke & Kühn (1987) show that there are different ordered and non-ordered adamantane-structure compounds (zinc-blende patterns with or without superstructure lines) with homogeneity ranges which extend along the pseudobinary line given by (8*b*), and with no extension perpendicular to this line within the error limits of the chemical analysis. According to Boehnke & Kühn (1987), at 1023 K the homogeneity range of the α phase extends from $CuInSe_2$ up to 55·0 mol% In_2Se_3 at the most. The β phase exists between 66·5 and 79·0 mol% In_2Se_3 and the γ phase between 82·0 and 90·0 mol% In_2Se_3. Further, there is a δ phase, a disordered high-temperature modification of $CuInSe_2$ without clearly defined phase boundaries. Of the previously reported compounds $Cu_2In_4Se_7$ ($y = 66{\cdot}7\%$), $Cu_8In_{18}Se_{32}$ ($y = 69{\cdot}2\%$ if the composition is $Cu_8In_{18}Se_{31}$), $Cu_7In_{19}Se_{32}$ ($y = 73{\cdot}1\%$), $CuIn_3Se_5$ ($y = 75\%$) and $CuIn_5Se_8$ ($y = 83{\cdot}3\%$), the first four belong to the β phase and the last one, obviously, to the γ phase (for references see Boehnke & Kühn, 1987). All these studies were made on polycrystalline powder samples.

Single-crystal studies of the β phase with composition $Cu_{0{\cdot}39}In_{1{\cdot}20}Se_{2{\cdot}00}$ ($x = 0{\cdot}6$ or $y = 75\%$ if the composition is $Cu_{0{\cdot}4}In_{1{\cdot}1}Se_2$) and of the δ phase with composition $Cu_{0{\cdot}46}In_{1{\cdot}18}Se_{2{\cdot}00}$ ($x = 0{\cdot}54$ or $y = 72\%$) have been published by Hönle, Kühn & Boehnke (1988).* The latest single-crystal structure study was made on $Cu_{0{\cdot}875}In_{1{\cdot}042}Se_2$ ($x = 0{\cdot}125$ or $y = 54{\cdot}35\%$) (Hönle, Kühn & Boehnke, 1989). All the compositions mentioned so far agree with the valence-electron rules given above.

At variance with the valence-electron rules is the In_2Se_3 content of the lower limit of the homogeneity range of the α phase which should be at $y = 50\%$, corresponding to composition $CuInSe_2$. According to Boehnke & Kühn (1987) this limit occurs, however, at the composition $Cu_{1{\cdot}05}In_{0{\cdot}95}Se_{1{\cdot}95} \equiv 52{\cdot}5\%$ Cu_2Se + 47·5% In_2Se_3† ($y = 47{\cdot}5\%$), *i.e.*, in this case we have $VEC = 3{\cdot}94_9 < 4$. In a recent review Haneman (1988) quoted a phase diagram due to Ciszak with a rather broad homogeneity range of the α phase at 1053 K from 43 to 53 mol% In_2Se_3.

Recently, Zahn & Paufler (1988) determined the type of intrinsic defects present in nonstoichiometric $CuInSe_2$ using the X-ray diffraction method. They found vacancies on In sites and In atoms on Cu sites. They studied three samples, the third at different temperatures and obtained the following results for the site occupations (with the name of the site written as a superscript):

Sample		Composition
1		$Cu^{Cu}_{0{\cdot}92\pm0{\cdot}02}In^{Cu}_{0{\cdot}05\pm0{\cdot}02}In^{In}_{0{\cdot}95\pm0{\cdot}01}Se_2$
2		$Cu^{Cu}_{0{\cdot}94\pm0{\cdot}03}In^{Cu}_{0{\cdot}05\pm0{\cdot}02}In^{In}_{0{\cdot}98\pm0{\cdot}02}Se_2$
3	80 K	$Cu^{Cu}_{0{\cdot}94\pm0{\cdot}02}In^{Cu}_{0{\cdot}05\pm0{\cdot}01}In^{In}_{0{\cdot}95\pm0{\cdot}02}Se_2$
3	190 K	$Cu^{Cu}_{0{\cdot}95\pm0{\cdot}03}In^{Cu}_{0{\cdot}05\pm0{\cdot}01}In^{In}_{0{\cdot}94\pm0{\cdot}02}Se_2$
3	300 K	$Cu^{Cu}_{0{\cdot}95\pm0{\cdot}03}In^{Cu}_{0{\cdot}06\pm0{\cdot}02}In^{In}_{0{\cdot}95\pm0{\cdot}02}Se_2$.

* The positional atom coordinates given in the publication for the δ phase apply to a compound with the slightly different composition $Cu_{0{\cdot}54}In_{1{\cdot}15}\square_{0{\cdot}31}Se_2$ ($x = 0{\cdot}46$ or $y = 68\%$). In the structure of the β phase there are vacancies on the cation and, surprisingly, also on the anion sites.

† Boehnke & Khün (1987) state that the chemical analyses of the Cu, In and Se contents are each accurate within about 4%.

Considering the given experimental standard deviations, all compositions agree with the theoretical composition $Cu_{0\cdot94}In_{1\cdot02}\square_{0\cdot04}Se_2$ ($x = 0\cdot06$ or $y = 0\cdot52$). Note that the valence-electron rules do not allow predictions concerning the details of the site occupation.

It remains for us to explain why one finds, as mentioned above, an adamantane structure with $Cu_{1\cdot05}In_{0\cdot95}Se_{1\cdot95}$ where $VEC = 3\cdot94_9 < 4$; this means that there are not sufficient valence electrons available for each atom to form an sp^3 hybrid and a tetrahedral structure should not form at all.

To explain this experimental result we shall consider two hypotheses:

(*a*) a possible deviation from the valence-electron rules;

(*b*) a possible uncertainty concerning the structure, the composition and the valence-electron contribution of the elements.

It is generally admitted that minimal deviations from the exact *VEC* value can be locally tolerated without a destabilization of the structure. This excess or deficiency of the bonding electrons will introduce changes in the electrical and optical properties of the compound. This has been confirmed for $CuInSe_2$ where annealing either under maximum or under minimum Se pressure allows a switch of conductivity from *p* type to *n* type (Massé & Redjai, 1986). The existence of Se-atom vacancies has been suggested from luminescence spectra (Massé & Redjai, 1986) as well as from an estimation of vacancy formation energies (Neumann, 1983). No numerical values for the change in composition were given in these papers; however, one can obtain an idea from the exact studies of the homogeneity range of GaP which can exist with an excess of Ga (Jordan, von Neida, Caruso & Kim, 1974). At 1273 K the composition of the Ga-rich side of the homogeneity range is $Ga_{0\cdot5001}P_{0\cdot4999}$ and, close to melting point, $Ga_{0\cdot5002}P_{0\cdot4998}$. That means the *VEC* value is 3·9998 or 3·9996 instead of 4·0 which can be expressed by $\Delta_{VEC}/VEC = 0\cdot5 \times 10^{-4}$ and $1\cdot0 \times 10^{-4}$, respectively. In the case of $Cu_{1\cdot05}In_{0\cdot95}Se_{1\cdot95}$, however, one calculates that $\Delta_{VEC}/VEC = 1\cdot275 \times 10^{-2}$. This means that the deviation is here 100 times larger and this would correspond to a quite different level of deviation from the valence-electron rules, which up to now has never been observed. One might also remember the above given examples where such gross deviations from the expected *VEC* served to indicate errors in composition or structure (for example $\Delta_{VEC}/VEC = 2\cdot5 \times 10^{-2}$ for In_4SnS_4).

We shall now consider the second hypothesis which relates to a possible uncertainty concerning the composition and the structure. Unfortunately, the chemical analyses of the components of this compound are accurate only to 4%. There is always the possibility of an impurity effect. It has been pointed out by von Bardeleben (1986) that extrinsic point defects, in particular the omnipresent contaminant iron, can be expected to substitute for the cation. Even in very small quantities these Fe atoms will influence the Fermi levels and the physical properties. Although an impurity effect cannot be excluded, this is certainly not enough to explain the large *VEC* deviation of $Cu_{1\cdot05}In_{0\cdot95}Se_{1\cdot95}$.

In an analogy to the interpretation of the forbidden homogeneity range in $CuGaS_2$, first stated by Kokta, Carruthers, Grasso, Kasper & Tell (1976), one might also consider the possibility that the Cu-rich '$CuInSe_2$' samples are not really single phase. Finely dispersed second-phase Cu_9Se_5 precipitates would be difficult, if not impossible, to recognize by X-ray diffraction methods.

There is the other possibility that some of the In atoms are no longer tetrahedrally coordinated and that the tetrahedral structure equation is not applicable anymore. To corroborate this viewpoint one might consider the structure of γ-In_2Se_3 (Likforman, Carré & Hillel, 1978) where some of the In atoms are tetrahedrally coordinated but others have five neighbours. It should be added that the Se atoms themselves have a simple hexagonal close-packed arrangement and it would have been perfectly possible for all the In atoms to occupy the tetrahedral interstices and thus form an adamantane structure. There are other examples, such as $Zn_3In_2S_6$ or $(Zn,In)_4S_3Se_2$, where some of the In atoms are tetrahedrally but others octahedrally coordinated, although an arrangement with *all* cations in tetrahedral interstices would not require any modifications or change of the anion framework.

There might also be a problem with the tetrahedral coordination of the Cu atoms. For example, Cu_2Se with $VEC_A = 8$ should crystallize in the anti-CaF_2-type structure with a cubic close-packed arrangement of Se atoms and Cu atoms in the tetrahedral interstices. Surprisingly, Cu_2Se does not exist, instead a compound Cu_9Se_5 is formed (Heyding & MacLaren Murray, 1976) characterized by a cubic close-packed anion arrangement as above but with only 72% of the Cu atoms in the tetrahedral interstices, the remaining Cu atoms having been displaced towards the triangular faces.

To resolve the $Cu_{1\cdot05}In_{0\cdot95}Se_{1\cdot95}$ puzzle a new experimental study is needed where a single crystal is used to determine the crystal structure and where the exact composition of the same single crystal is measured by high-precision microprobe analysis.

We have given here some examples of how the controlling equations for adamantane-structure compounds and the corresponding master diagram can be used as a guide to localize quickly the compositions of possible adamantane-structure compounds

in various ternary systems. We have also seen how these equations and the diagram can be applied to check experimental data. The great wealth of experimental results which have been published since the first introduction of the valence-electron rules for adamantane-structure compounds a quarter of a century ago happily does not require any modifications of the valence-electron rules. On the contrary, deviating experimental results have eventually always been shown to be incorrect.

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A Low-Temperature Structural Phase Transformation in CuAgS

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Abstract

The symmetry and crystal structure of CuAgS have been examined by electron and X-ray diffraction between 13 and 298 K. The room-temperature space group has been deduced by convergent-beam electron diffraction to be $Cmc2_1$ (No. 36). A second-order phase transition has been found to occur at approximately 250 K and below the transition the space group is $Pmc2_1$ (No. 26). The structures at 298 and ~120 K have been refined by single-crystal X-ray diffraction and the Rietveld method has been used to refine the structure at 13 K from powder

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