

A NOTE ON CHOICE OF END MEMBERS IN REPRESENTING CERTAIN SYSTEMS AND ON A POSSIBLE ALTERNATIVE TO VEGARD'S RULE

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ABSTRACT

Correction of the statement of end-member formulas in such systems as $\text{AgBiS}_2\text{-PbS}$, making them consistent with substitutions in mix-crystal series, eliminates the reported negative deviations from Vegard's rule in many systems. Tests of Vegard's own data for the system Cu-Au plus modern data for the same system and for many selected systems, including the system $\text{AgSbTe}_2\text{-PbTe}$, suggest that volume additivity rather than linear additivity (Vegard's rule) best approximates the relations in some mix-crystal series.

SOMMAIRE

En modifiant l'énoncé des formules de pôle dans une série de solutions solides, telle que $\text{AgBiS}_2\text{-PbS}$, de façon à rendre ces formules compatibles avec les substitutions du système, on élimine les prétendus écarts négatifs à la règle de Vegard dans beaucoup de séries. A la suite de tests effectués sur les données mêmes de Vegard concernant le système Cu-Au , ainsi que des données plus récentes sur ce même système et de nombreux autres systèmes choisis, en particulier $\text{AgSbTe}_2\text{-PbTe}$, on se rend compte que l'additivité des volumes se vérifie avec une meilleure approximation que l'additivité des longueurs (règle de Vegard) dans certaines séries de solutions solides.

(Traduit par la Rédaction)

INTRODUCTION

Several authors (Wernick 1960a,b; Van Hook 1960; and most recently, Hoda & Chang 1975), in dealing with such systems as PbS-AgSbS_2 (galena — α -miargyrite) and PbS-AgBiS_2 (galena — α -matildite), have plotted chemical and physical relations for mix-crystal series using disparate formulations for the end members. Van Hook (1960, p. 778) stated "The system is represented as $\text{AgBiS}_2\text{-PbS}$ to conform with the binary join in the ternary system, although the assumed substitution, $\text{Ag}^+, \text{Bi}^{3+} = 2\text{Pb}^{2+}$, indicates that the system should be considered as $\text{AgBiS}_2\text{-2PbS}$." In a footnote to this sentence Van Hook states "Representation as $\text{AgBiS}_2\text{2PbS}$ results in a positive deviation from Vegard's Law rather than negative as in Fig. 9." (Note: a printer's error in the quoted footnote has

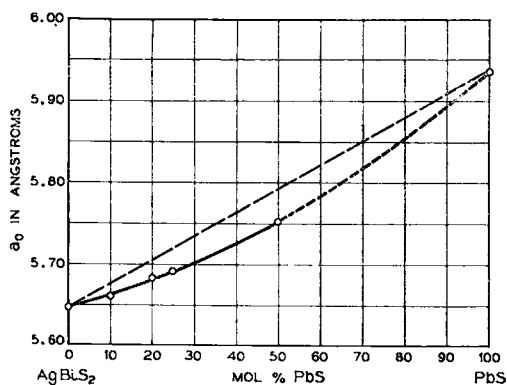
here been corrected). Such systems should not only be "considered" in the manner indicated by Van Hook, they should also be represented in this manner, especially when correlation of physical properties with composition, e.g. variation of lattice constants with composition, "Vegard's Law", is involved.

Unfortunately, Van Hook published no numerical values, only a diagram. Hoda & Chang (1975, Table 2) published data for six intermediate members of the system $\text{AgBiS}_2\text{-PbS}$. They stated that the variation in a_0 agrees "well with Van Hook's results", though only a qualitative comparison can have been possible. They reported cell dimensions only to hundredths of an ångström, inadequate for a test of agreement with Vegard's rule. Moreover, their data show differences of -0.016 , -0.020 and -0.019Å at the three points where the compositions of their materials match those of Wernick (1960b, Table 2 and Fig. 6) who reported cell dimensions for four intermediate members of the series.

RESTATEMENT OF COMPOSITIONAL RELATIONS

Figure 1 shows Wernick's diagram for what he refers to as the " $\text{AgBiS}_2\text{-PbS}$ system". It also shows a plot of the relations "considered" in the manner advocated by Van Hook, for which the form $\text{AgBiS}_2\text{-PbPbS}_2$ is preferred. Figure 1 has been shown (Pabst 1960) and published (Pabst 1975) before but with only minimal comment. Wernick and others have noted the apparent negative departures from Vegard's rule suggested by such plots as that shown in the upper part of Figure 1 and have offered various explanations of such departures. As can be seen from this example, negative departures may be the result of inappropriate formulation. Comparable positive deviations would arise if the end member whose formula must be modified in the manner in which the galena formula has here been modified were the end member with the smaller cell edge.

Vegard & Dale (1928) used the system Cu-Au , among others, to illustrate the rule. In this simple case one metal atom substitutes for another and no problem of formulation arises.



Lattice constants at 25° C. for the cubic β -phase in the AgBiS_2 - PbS system.

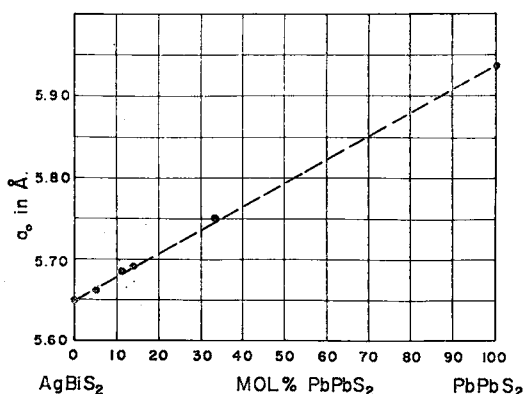


FIG. 1. Top: Figure 6 from Wernick (1960b, p. 596). Bottom: Replotting of same data after change to consistent formulas for the two components.

In many other cases, such as those here under consideration, end members must be chosen to correspond to the postulated substitutions. One

might, for instance, choose cell contents as end members in which case the formulas given in the lower part of Figure 1 should both be doubled.

The "positive deviation" mentioned by Van Hook in the footnote quoted above is so slight in this and many other cases that it cannot be shown adequately in a diagram. Table 1 shows the data of Wernick (1960b — Table 2) for the system AgBiS_2 - PbS with some additions. In the table "linear variation" corresponds to points on the straight dashed line of Wernick's diagram above the data points on his curve (upper part of Fig. 1), entered in the table in the column headed "observed Wernick". The a_0 values entered in the columns headed "linear additivity" and "volume additivity" have been calculated on the basis of the modified formulation. There is, indeed, a small positive deviation of the observed values of a_0 from the newly calculated values, possibly within the limits or error. Wernick *et al.* (1958) reported on the variation of cell dimensions with composition in six related "pseudo-binary systems" and found no marked negative deviations, correction of the formulation not being required in any of these cases. In all but one of the six cases their figures show slight positive deviation similar to that recorded in Table 1.

AN ALTERNATIVE TO VEGARD'S RULE

Following Bloss (1952) one might assume a rule of volume additivity rather than additivity of cell dimensions (hereafter referred to as linear additivity) and calculate the corresponding cell dimensions for intermediate members. The results of such calculations for the system AgBiS_2 - PbS have been included in Table 1. It is seen that the differences are slight and that the

TABLE 1. CORRELATION OF LATTICE CONSTANTS WITH COMPOSITIONS FOR THE SYSTEM AgBiS_2 - PbS , α -MATILDITE-GALENA

mol %		a_0			mol %	
Wernick's formulation	"linear variation" Wernick	observed Wernick	linear additivity	volume additivity	modified formulation	
AgBiS_2	PbS				AgBiS_2	PbPbS_2
100		5.648Å			100	
90	10	5.660	5.663	5.664	94.74	5.26
		(-0.017)	-0.003	-0.004*		
80	20	5.684	5.680	5.682	88.89	11.11
		(-0.022)	+0.004	+0.002)		
75	25	5.690	5.689	5.691	85.72	14.28
		(-0.030)	-0.001	+0.001)		
50	50	5.751	5.744	5.747	66.67	33.33
		(-0.041)	+0.007	+0.004)		
	100	5.936				100

Data from Wernick (1960b, Table 2)

*Figures in brackets are the differences between the observed and calculated a_0 .

values based on volume additivity are higher, suggesting that positive deviations from a straight-line relation may be indicative of volume additivity.

The values based on linear additivity and on volume additivity differ so little in cases in which the dimensions of the end members are close that no discrimination is possible with data of the usual accuracy. This situation has been dealt with "theoretically" by Zen (1956) who remarked that it is "intuitively obvious". Bethke & Barton (1961, p. B270, col. 1), after referring to Zen, state: "For most systems the difference between Vegard's Law (additive cell edge) and ideal behavior (additive cell volume) is too small to be detectable by standard procedures." In a later paper Barton & Bethke (1971) state in their abstract that "Reevaluation of our earlier published relationship between unit-cell edge and composition of CdS-bearing galena suggests that unit-cell volume, rather than unit cell edge, is a linear function of composition" whereas in the text (p. 2038) they state "It is apparent that both relationships describe our data equally well."

Appropriate systems must be chosen to test the relations. The cell dimensions of AgBiS₂ and PbS differ by only about 5%. On the other hand, those of Cu and Au differ by about 13% so that Vegard & Dale might have had suitable data for discriminating between linear and vol-

ume additivity. From their discussion it seems that they did not consider the latter.

Vegard & Dale (1928) investigated five pairs of cubic isostructural materials. They found continuous mix-crystal series between three of these pairs, Pb(NO₃)₂-Ba(NO₃)₂, Cu-Ni, and Cu-Au. The last of these is best suited for testing correlation of cell dimensions with composition because the percentage difference in cell dimensions of the end members is by far the greatest in this case. Table 2A shows the Vegard & Dale results copied from their "Tabelle IV" and additionally cell dimensions of the intermediate members calculated on the basis of volume additivity. The figures in brackets show the differences between observations and calculations, clearly indicating that for this system volume additivity is a better approximation than linear additivity. The numbers given by Vegard & Dale, though stated to be in Å units are, of course, in *kX* units. Moreover, their measurements would not satisfy present-day expectations of accuracy. Table 2B shows comparable calculations using cell dimensions for Cu and Au reported by Batchelder & Simmons (1965) (quoted from CRYSTAL DATA, 3rd ed., there converted from *kX* to Å) and data for Cu-Au disordered alloys quenched from 450°C reported by Davies & Funes (1961) (as given in STRUCTURE REPORTS 26, p. 135, Fig. 48). The results of these calculations support the

TABLE 2. CORRELATION OF LATTICE CONSTANTS WITH COMPOSITION FOR THE SYSTEM Cu - Au.

A				B			
Mol %	a_0			Mol %	a_0		
	observed	calculated from Vegard's law	calculated for volume additivity		observed	calculated from Vegard's law	calculated for volume additivity
Au				Au			
0	3.613 <i>kX</i>			0	3.61529Å		
15	3.695	3.683 (+0.012)	3.691 (+0.004)*				
30	3.775	3.753 (+0.022)	3.765 (+0.010)				
50	3.880	3.847 (+0.033)	3.861 (+0.019)	65	3.9431	3.9167 (+0.0264)	3.9290 (+0.0141)*
65	3.944	3.917 (+0.027)	3.929 (+0.015)	69	3.9571	3.9352 (+0.0219)	3.9467 (+0.0104)
80	3.997	3.987 (+0.010)	3.995 (+0.002)	75	3.9853	3.9631 (+0.0222)	3.9730 (+0.0123)
90	4.034	4.033 (+0.001)	4.038 (-0.004)	80	4.0086	3.9862 (+0.0224)	3.9946 (+0.0140)
100	4.080			100	4.07897		

A. Data in first three columns quoted from Vegard & Dale (1928, Tabelle IV)

B. a_0 for Cu and Au from Batchelder & Simmons (1965).
 a_0 for Cu-Au alloys quenched from 450 C from Davies & Funes (1961).

*Figures in brackets are the differences between the observed and calculated a_0 .

TABLE 3. CORRELATION OF LATTICE CONSTANTS WITH COMPOSITION FOR THE SYSTEM AgSbSe_2 - PbTe

mol %		a_0			mol %	
Wernick's formulation		"linear variation" Wernick	observed Wernick	linear additivity	volume additivity	modified formulation
AgSbSe_2	PbTe					AgSbSe_2 PbPbTe_2
100			5.786 $\overset{\circ}{\text{A}}$			100
90	10	5.853 (-0.025)	5.828	5.821 +0.007	5.825 +0.003)	94.74 5.26
75	25	5.954 (-0.060)	5.894	5.882 +0.012	5.892 +0.002)	85.72 14.28
50	50	6.122 (-0.104)	6.018*	6.010 +0.008	6.027 -0.009)*	66.67 33.33
25	75	6.291 (-0.081)	6.210	6.190 +0.020	6.207 +0.003)	40.00 60.00
	100		6.459			100

Data from Wernick (1960a, Table 11).

*It seems probable that the observed value quoted here or the stated composition may be slightly in error. See text for comment.

conclusions drawn from the much older data.

The other binary system dealt with by both Hoda & Chang and by Wernick (1960b), AgSbSe_2 - PbS (α -miargyrite — galena), invites comparison but the data appear unsuited for any test because of the marked disagreement in the value of a_0 of α -miargyrite given by Hoda & Chang, 5.603 $\overset{\circ}{\text{A}}$, with the values given by Wernick (1960b), 5.647 $\overset{\circ}{\text{A}}$, and by Graham (1951), 5.653 $\overset{\circ}{\text{A}}$. There are also marked discrepancies in reported dimensions for the two intermediate compositions which are common to the two tabulations.

In his conference contribution Wernick (1960a) reported on the six binary systems between AgBiSe_2 , AgSbSe_2 , AgSbTe_2 , and PbSe or PbTe . In all but one of these systems, AgSbTe_2 - PbSe , in which the difference in dimensions of end members is very small (0.75%) he reported "large negative deviations from Vegard's law". In each of these five cases the deviations can be reduced or eliminated by correcting the formulation of the end members. Calculations to discriminate between the appropriateness of the assumptions of linear or volume additivity were carried out for each of these five systems. In four cases the results favored volume additivity and in the remaining case, AgBiSe_2 - PbTe (Wernick 1960a, table VI), no clear indication can be found because the calculated values for the two assumptions, in part, lie on opposite sides of the observed values and the differences are small.

Of these systems the one with the greatest relative difference (11.6%) in a_0 of the end members, AgSbSe_2 - PbTe (Wernick, 1960a, Ta-

ble II), will yield the most sensitive test for discriminating between linear and volume additivity. The results of the calculations for this series were chosen for presentation in Table 3 in spite of a blemish in the data. It is easily seen that the observed a_0 for the 50% composition of Wernick (66.67-33.33% as corrected) is not in accord with the other values. Possibly through misprint or other oversight a faulty value was introduced. If the apparently faulty value is arbitrarily replaced by 6.030, the associated differences in the adjoining columns become -0.092, +0.020 and +0.003, fitting nicely with the other tabulated differences. Such an adjustment of the numbers is also indicated by fitting a three-term polynomial to Wernick's data in such a manner as to represent a curve constrained to run through 5.786 $\overset{\circ}{\text{A}}$ at 100% AgSbSe_2 . However, an error in the stated composition of about 2% would also account for the odd values of the tabulated differences at one point.

SUMMARY

It has been shown that the large apparent negative deviations from Vegard's rule reported by several authors are the result of faulty formulation of end members. Upon reformulation the deviations are reduced or may be changed to slight positive deviations. Several systems have been tested for correlation of cell dimensions with composition on the basis of assumption of volume additivity. For the classic case of Cu-Au it seems clear that volume additivity is a closer approximation to the existing rela-

tions than additivity of cell constants. The same is true for the system $\text{AgSbSe}_2\text{-PbTe}$ (see Table 3) though the case is marred by an inconsistency in the reported a_0 for one point. In some other cases, not reported here in detail, the observed values of a_0 lie almost midway between the calculated values corresponding to linear and to volume additivity so that no discrimination is possible.

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