Variation with composition of the E_0 and $E_0 + \Delta_0$ gaps in ZnS_xSe_{1-x} alloys

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Reflectivity measurements were made to determine the variation with composition of the lowest gap E_0 together with its spin-orbit-split gap $E_0 + \Delta_0$ in ZnS_xSe_{1-x} at room temperature. The variation of these gaps indicates that ZnS_xSe_{1-x} is an amalgamation-type alloy, at least for these gaps, contrary to a previous suggestion of a persistence type. The bowing parameters of the E_0 and $E_0 + \Delta_0$ gaps are determined to be 0.630 ± 0.030 and 0.596 ± 0.023 eV, respectively. The variation with composition of the spin-orbit splitting Δ_0 tends to be convex as in the case of $ZnSe_xTe_{1-x}$ alloys. The negative bowing of Δ_0 may be interpreted in terms of the virtual-crystal approximation.

I. INTRODUCTION

It is well known that the energy gaps in alloys of typical semiconductors with zinc-blende structure vary gradually with composition change. This type of alloy is referred to as an amalgamation type.[1] The energy gaps in these alloys vary as a quadratic function in composition. There is another type of alloy in which the respective gaps originating from the end-point compounds remain nearly stationary in energy with composition change. For example, exciton levels in halogen-substituted alkali halides such as KBr-KCl (Ref. 1) belong to this type. An early measurement of diffuse reflectance on powders of ZnS_xSe_{1-x} (Ref. 2) has shown that the lowest gap energy varies approximately linearly with composition. More recent reflectivity measurements on crystals of this alloy system have indicated that it belongs to the persistence type.[3]

The purpose of this work is twofold: (i) to determine whether the ZnSe-ZnS system forms persistence-type alloys as reported previously[3] or amalgamation-type alloys like a number of III-V and II-VI compound alloys; (ii) (the main subject in this work) to determine a bowing parameter of the lowest gap together with that of its spin-orbit-split gap. We believe that the bowing of energy gaps is a significant quantity, useful to check the point of view on which theoretical approximations are based. Two opposite approximations[4-7] are currently used; one is to include disorder effects resulting from fluctuations in the crystal potentials, the other is to exclude these effects. It is not known conclusively whether disorder has a significant role in the bowing of the energy gaps in semiconductor-alloy systems. Hence, our main object is to present experimental evidence which clarifies the nature of the effect of disorder on the optical spectrum of semiconductor alloys.

II. EXPERIMENTAL

Single crystals of ZnS_xSe_{1-x} were grown from the melt through the whole range of composition. In Ref. 3, crystals of ZnS_xSe_{1-x} have been grown by an iodine-vapor transport technique. We prefer the high-pressure melting method, because we were familiar with it. We have prepared various II-VI alloy systems such as CdTe-ZnTe,[8] ZnTe-ZnSe,[9] and CdSe-CdS by this method. Fabrig *et al.*[10] reported the crystal growth of ZnS_xSe_{1-x} by the same method. The as-grown boule, 15 mm in diameter by 30 mm, is composed of several single-crystal blocks. The largest size of a cleaved single-crystal plane was 5×8 mm. An x-ray analysis showed that the crystals of the alloys had the zinc-blende structure, although the alloys with x larger than 0.9 showed a short-range twin structure which is typically observed in ZnS grown from the melt.[11] The composition x was determined from lattice-constant measurements, on the basis of Vegard's law. The variation in x through the whole boule is about 4%. Its value in a single-crystal block is $\pm 0.5\%$.

Cleaved planes were used in the reflectivity measurements. Some cases of the ZnSe-rich alloys, have a mosaic structure similar to that often observed in the melt-grown crystals of ZnSe.

Reflectivities were measured at room temperature in the region from the lowest gap energy up to 6.4 eV at near-normal incidence, using a Shimazu-40R spectrophotometer of a double-beam prism-grating type with a reflectivity-measurement attachment of our design.

III. RESULTS

Figure 1 shows the reflectivities measured for alloys with various composition. The peak positions in the spectra are shown by arrows in the

figure. They were determined to within ±0.01 eV from one measurement to the other for the same sample and/or one sample to the other with the same composition, except for $x=0.62$. In the case of $x=0.62$, the experimental errors were within ±0.03 eV. Therefore, the data for this sample will not be used in the following calculations of the least-squares fits with the observed data.

The low-energy pair of peaks appearing in Fig. 1 correspond to the E_0 and $E_0+\Delta_0$ gaps, where the former is identified with the lowest gap and the latter with its spin-orbit-split gap. The high-energy pair corresponds to the E_1 and $E_1+\Delta_1$ gaps, which are ascribed to transitions at the Λ points in the Brillouin zone. The doublet structure of these gaps was resolved only for x less than 0.68, as can be seen in the figure. This pair will not be considered in this work.

The peak positions for the E_0 and $E_0+\Delta_0$ gaps are plotted as functions of x in Fig. 2. This figure indicates that they vary gradually with composition from ZnSe to ZnS. No evidence of the persistence-type alloys is observed at least for these gaps. It is noted that the peak position of the E_1 gap for ZnS-rich alloys may remain stationary. More measurements will be needed to verify this. These results show that the ZnSe-ZnS system is of the amalgamation type, as are a number of typical alloy systems with zinc-blende structures.

Also, Fig. 2 shows that the observed points for $x=0$ and 1.0 seem to occur at slightly lower energies than those expected from the quadratic variation in x. Therefore, data for these two samples will not be included in the least-squares fits unless otherwise indicated. The fittings to a quadratic expression in x with the observed data for the E_0 and $E_0+\Delta_0$ gaps give

$$E_0 = 2.721 + 0.352x + 0.630x^2 \text{ eV},$$

$$E_0+\Delta_0 = 3.159 + 0.060x + 0.596x^2 \text{ eV}.$$

The solid lines in this figure are the results based on the above equations. The bowing parameters, which are given by the coefficients of the quadratic term in the above equations, are determined to be 0.630 ± 0.030 and 0.596 ± 0.023 eV for the respective gaps. The bowing of the lowest

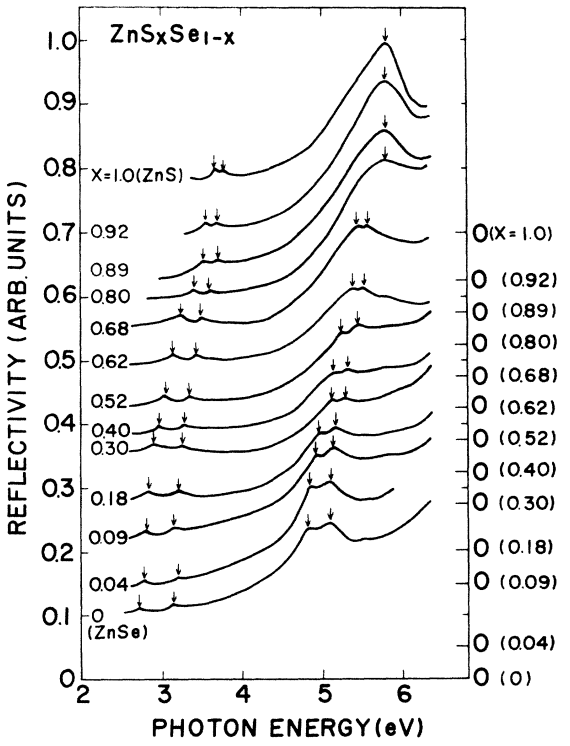


FIG. 1. Reflectivity spectra of ZnS_xSe_{1-x} alloys at room temperature. Arrows in the figure are the peak positions in the spectra.

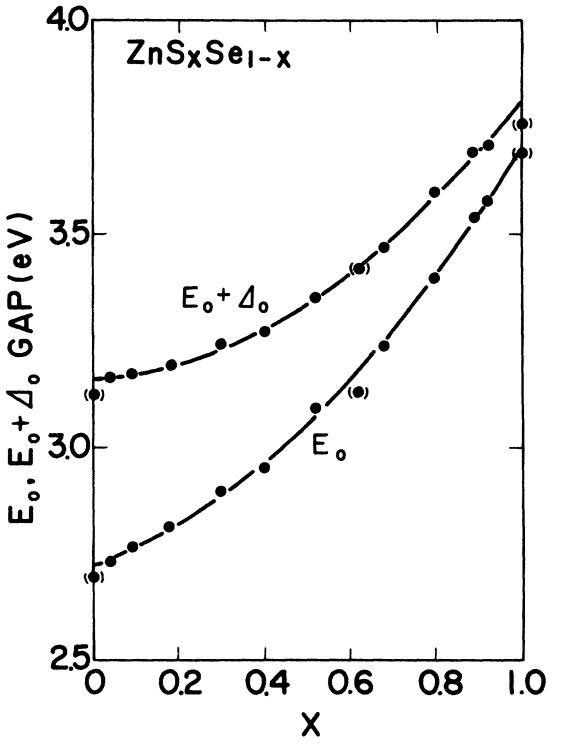
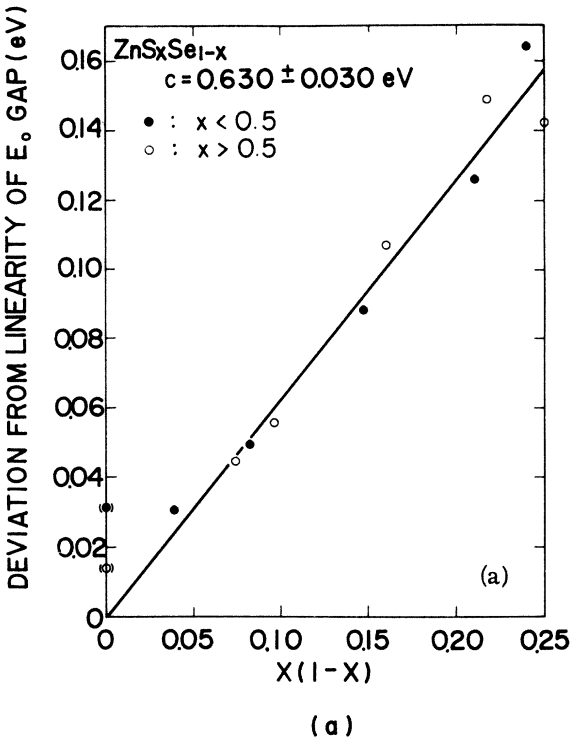


FIG. 2. Peak positions of the E_0 and $E_0+\Delta_0$ gaps as a function of composition x. Solid lines represent the calculations by the equations $E_0 = 2.721 + 0.352x + 0.630x^2$ and $E_0+\Delta_0 = 3.159 + 0.060x + 0.596x^2$, which were given by the least-squares fits with the observed data. The observed points in parentheses in the figure are not included in the fit.



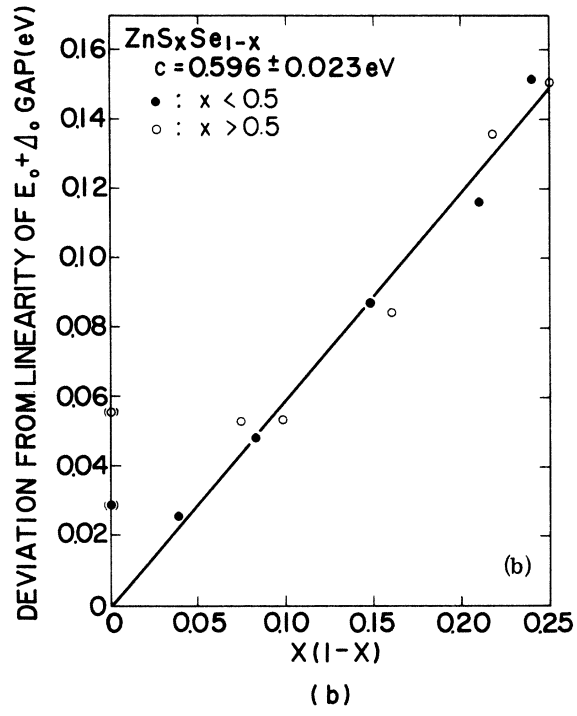


FIG. 3. Deviation from linearity of the (a) E_0 and (b) $E_0 + \Delta_0$ gaps as a function of $x(1-x)$. Solid lines in the figure represent the calculations using bowing parameters of 0.630 and 0.596 eV for the respective gaps. The observed points in parentheses in the figure are not included in the fittings.

gap without spin-orbit splitting is 0.62 eV, in good agreement with the value of 0.60 eV, calculated using an empirical pseudopotential method based on the virtual-crystal approximation,[5] in which the disorder effects were not taken into account. Also, the dielectric method with the disorder effects explains this bowing.[7]

The deviation from linearity, which is given by $\delta E_0 = E_{0L} - E_0 = cx(1-x)$, is plotted in Fig. 3(a), where E_{0L} is the linear gap and is calculated using parameters given by the least-squares fit. A similar plot for the $E_0 + \Delta_0$ gap is presented in Fig. 3(b). The good linear relation between δE_0 or $\delta(E_0 + \Delta_0)$ and $x(1-x)$ is seen for both gaps.

Figure 4 shows the observed data of the spin-orbit splitting Δ_0 as a function of x. The least-squares fit with the observed data gives

$$\Delta_0 = 0.436 - 0.261x - 0.067x^2 \text{ eV}.$$

The result based on this equation is represented by a solid line in the figure. The bowing parameter c of Δ_0, thus obtained, is $c = -0.067 \pm 0.028$ eV. It is very small compared with that of $ZnSe_xTe_{1-x}$, for which $c = -0.59$ eV was given from electroreflectance measurements.[12] We believe that the variation with composition of ZnS_xSe_{1-x} is convex as in $ZnSe_xTe_{1-x}$. This convex behavior is opposite to the concave behavior observed for several III-V alloy systems.[13]

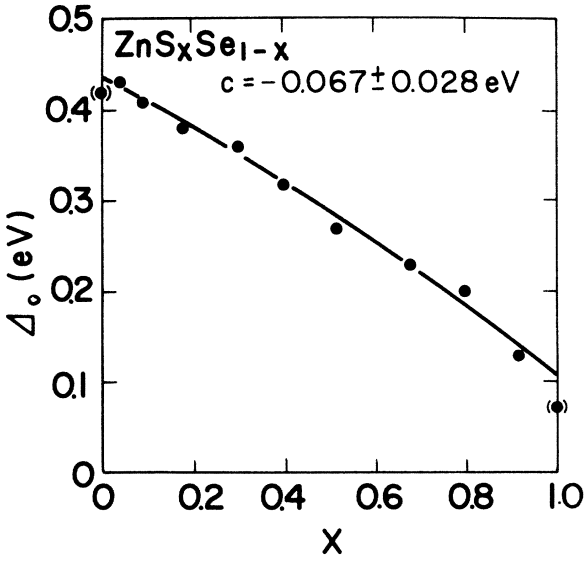


FIG. 4. Spin-orbit splitting Δ_0 as a function of x. A solid line in the figure represents the calculation by the equation $\Delta_0 = 0.436 - 0.261x - 0.067x^2$, which is given by the least-squares fit with the observed data. The observed points in parentheses in the figure are not included in the fitting.

TABLE I. Summary of the observed and calculated values of the E_0 and $E_0+\Delta_0$ gaps together with the spin-orbit splitting Δ_0 for ZnSe and ZnS. The calculated values are from the quadratic function in x given by the least-squares fits with the observed data for ZnS_xSe_{1-x} alloys. Also, data from electroreflectance measurements on $ZnSe_xTe_{1-x}$ are included for ZnSe. All entries are in eV.

		Present work		Electroreflectance [a]	
		Observed	Calculated	Observed	Calculated
ZnSe	E_0	2.69 ± 0.01	2.721 ± 0.006	2.713 ± 0.005	2.706 ± 0.024
	$E_0+\Delta_0$	3.12 ± 0.01	3.159 ± 0.004	3.136 ± 0.005	3.146 ± 0.009
	Δ_0	0.42 ± 0.01	0.436 ± 0.005	0.425 ± 0.005	0.440 ± 0.032
ZnS	E_0	3.69 ± 0.01	3.703 ± 0.044		
	$E_0+\Delta_0$	3.76 ± 0.01	3.815 ± 0.034		
	Δ_0	0.07 ± 0.01	0.108 ± 0.040		

[a] See Ref. 12.

IV. DISCUSSION

The peak positions in the reflectivity spectra are 2.69 and 3.12 eV in ZnSe and 3.69 and 3.76 eV in ZnS for the E_0 and $E_0+\Delta_0$ gaps, respectively. They are in good agreement with those reported previously.[14-18] However, the least-squares fits with the observed data of ZnS_xSe_{1-x} alloys predict slightly larger values for both ZnSe and ZnS, as one can see from Figs. 2 and 3. The fits between experiments and calculations are excellent for the alloys. Table I summarizes the observed values for ZnSe and ZnS together with the calculations using the quadratic fits with the alloy data. For a comparison, data deduced from electroreflectance measurements on $ZnSe_xTe_{1-x}$ are also included for ZnSe. The table shows that the peak positions of the reflectivity spectra have a tendency to be lower in energy than those obtained by the other methods, in particular for the $E_0+\Delta_0$ gap. This is the reason why we did not include the data for the end-point compounds in the quadratic fits. Figure 5 shows the deviations from linearity of the E_0 and $E_0+\Delta_0$ gaps including the data of the end-point compounds. It should be noted that the fit is worse with some systematic deviation from the linear relation than that presented in Fig. 3 for the both gaps. This deviation cannot be interpreted by a suggestion proposed by Hill.[6] Hill indicated that the bowing parameter should be modified in terms of the lattice-constant change accompanied by alloying, i.e., $\delta E = cx(1-x) \times [a(0.5)/a(x)]^4$, where a is the lattice constant. The result of calculating δE for the E_0 gap by this equation is presented in Fig. 6. Although the observed data, which are shown by circles in the figure, are scattered considerably, no such trend of the deviation is seen.

The present results, which indicate that the calculations by the quadratic function deduced from the alloy data yield larger values than those observed for the end-point compounds ZnSe and ZnS, suggest strongly that the observed gaps of these end-point compounds are lowered by some effects. It is likely that this lowering effect is significant only in semiconductor alloys composed of compounds with rather large ionicity. A possible interpretation is excitonic effects. The electroreflectance spectra of $ZnSe_xTe_{1-x}$ (Ref. 12) measured at room temperature indicated that a structure attributed to excitonic transitions was observed only for ZnSe. No such evidence was observed by us even for the alloy with $x=0.97$. Fluctuations in the crystal potentials in the alloy

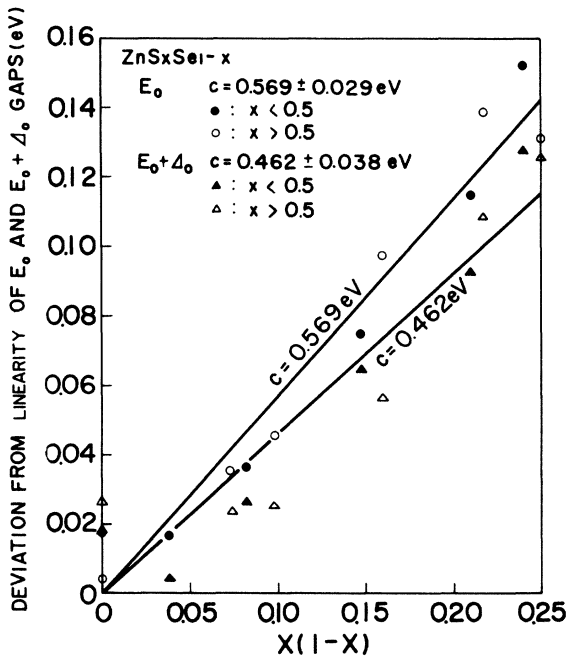


FIG. 5. Deviation from linearity of the E_0 and $E_0+\Delta_0$ gaps as a function of $x(1-x)$ including the observed data of $x=0$ and 1.0. Solid lines represent the calculations using the bowing parameters given by the least-squares fits.

may smear out the structure due to excitions. The difference in form factors between ZnSe and ZnTe is of order 0.01 Ry.[19] Several percent alloying results in fluctuations in the form factor with a magnitude of the same order as the excitonic binding energy of 0.028 eV for ZnSe or 0.04 eV for ZnS.[14,20,21] Thus, the excitonic evidence may be observed only for the end-point compounds in ZnS_xSe_{1-x} and $ZnSe_xTe_{1-x}$ alloys.

The observed spin-orbit splitting Δ_0 is 0.43 and 0.07 eV for ZnSe and ZnS, respectively. Quadratic fits to the observed data give splittings of 0.436 and 0.108 eV, respectively. The value for ZnSe is in good agreement with the reported value of 0.40–0.43 eV,[14,17,20,22] whereas the value for ZnS is larger than the reported values of 0.072 or 0.092 eV for the cubic or hexagonal modifications,[15,16,18,22-24] respectively. No reasonable explanation for this result can be given at this time.

The bowing of Δ_0 tends to be convex, although it is close to a linear variation. The linear least-squares fit yields a characteristic error in Δ_0 of 1.2 times that found from quadratic fitting. This may also indicate the quadratic variation of Δ_0 instead of the linear. The bowing parameter of Δ_0 obtained in this work may be explained in terms of the virtual-crystal approximation (VCA). On the basis of the VCA, the phenomenological expression for $\Delta_0(x)$ including lattice-constant change was given in Ref. 12. The bowing parameter given in Ref. 12 is as follows:

$$c = -[(\Delta_0 f\alpha)_{ZnSe} + (\Delta_0 f\alpha)_{ZnS}],$$

where f is a proportionality factor between the fractional change in Δ_0 and in the lattice constant and α is a measure of the lattice-constant change by

$$\delta\Delta_0/\Delta_0 = -f\delta a/a,$$

$$\alpha_{ZnSe} = 1 - a_{ZnS}/a_{ZnSe}, \quad \alpha_{ZnS} = 1 - a_{ZnSe}/a_{ZnS}.$$

The calculation gives $c = -0.015$ eV for $f_{ZnSe} = f_{ZnS} = 1$ and $c = -0.074$ eV for $f_{ZnSe} = 4$ and $f_{ZnS} = 1$, using Δ_0's for ZnSe and ZnS determined by the quadratic function. The satisfactory agreement of the observed bowing of $c = -0.067 \pm 0.028$ eV with the calculation may be obtained for the parameters of $f_{ZnS} = 1$ and $f_{ZnSe} = 3$–4. These values for f seem to be reasonable.[12,25] This result shows that the VCA may be valid in ZnS_xSe_{1-x} alloys for interpreting the bowing of the spin-orbit splitting of the lowest gap as well. The negligible effect of intraband transitions caused by disorders on the bowing of Δ_0 in ZnS_xSe_{1-x} can probably be explained in terms of the energy distribution of the valence-band density of states.[26] Disorder effects may be significant in $ZnSe_xTe_{1-x}$.[12]

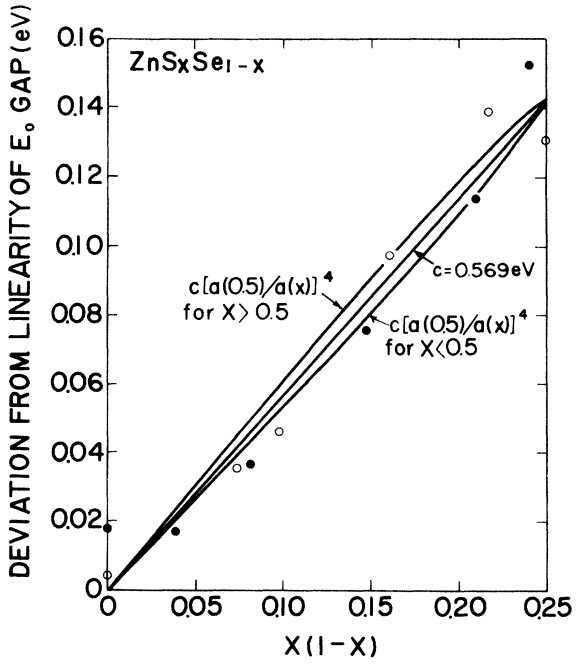


FIG. 6. Comparison of the experiment with the calculation of the deviation from linearity δE of the E_0 gap. The solid lines represent the results of calculations using the equations using the equation $\delta E = cx(1-x)[a(0.5)/a(x)]^4$ and $\delta E = cx(1-x)$, where c and a are the bowing parameter and the lattice constant, respectively.

It is concluded that the energies of the E_0 and $E_0 + \Delta_0$ gaps vary gradually with composition change, indicating that the alloys ZnS_xSe_{1-x} belong to the amalgamation type. The bowing of the respective gaps were determined to be $c = 0.630 \pm 0.030$ and 0.596 ± 0.023 eV. The variation of Δ_0 with composition is convex with a bowing of $c = -0.067 \pm 0.028$ eV. The negative bowing of Δ_0 can be explained in terms of the VCA.

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