

corresponding initial values  $\zeta_i$ . Substitution of the constant  $e_{ij}$  together with Eqs. (A3), (A4), (A8), and (A10) into Eq. (A2) yields the form of  $U_\lambda$  for final substitution into Eq. (C1) to give the desired expression for  $U_w$  as Eq. (7) in the text.

#### APPENDIX D. MAGNETIC ANISOTROPY RESULTING FROM AN APPLIED STRESS

The elastic strain components  $e_{ij}^\sigma$  resulting from the application of a linear stress are

$$e_{ii}^\sigma = \frac{\sigma\gamma_i^2}{C_{11}-C_{12}} - \frac{C_{12}\sigma}{(C_{11}-C_{12})(C_{11}+2C_{12})}, \quad (D1)$$

$$e_{ij}^\sigma = \frac{\sigma\gamma_i\gamma_j}{C_{44}} \quad \text{for } i \neq j,$$

where the applied stress is defined by the magnitude  $\sigma$

and the direction cosines  $\gamma_i$ . Since the  $e_{ij}^\sigma$  do not depend upon the magnetization, the only contribution to the magnetic anisotropy energy is through the magnetoelastic coupling energy  $U_\lambda^\sigma$ ,

$$U_\lambda^\sigma = U_\lambda^0 + U_\sigma. \quad (D2)$$

$U_\lambda^0$  is the magnetoelastic coupling energy for zero applied stress used in Appendixes A, B, and C.  $U_\sigma$  is the total contribution to the magnetic anisotropy energy due to the applied stress which, by analogy with Eq. (A2), may be expressed as

$$U_\sigma = F_{11}e_{xx}^\sigma + F_{22}e_{yy}^\sigma + F_{33}e_{zz}^\sigma + F_{12}e_{xy}^\sigma + F_{23}e_{yz}^\sigma + F_{13}e_{zx}^\sigma. \quad (D3)$$

Substitution of Eqs. (A3), (A4), (A8), (A10), and (D1) into Eq. (D3) finally gives  $U_\sigma$  as an explicit function of the magnetization direction cosines  $\alpha_i$  and the applied stress in Eq. (17) in the text.

## Anomalous Variation of Band Gap with Composition in Zinc Sulfo- and Seleno-Tellurides

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A monotonic variation of band gap with composition occurs for many binary solid solutions. Of some Group II-Group VI systems, ZnS-ZnSe shows this type of variation of band gap with composition, whereas ZnSe-ZnTe, ZnS-ZnTe show an anomalous minimum in a plot of band gap *versus* composition of the solid solution.

### INTRODUCTION

SOME measurements of the variation of band-gap energy with composition in isomorphous series of two-component solid solutions have been reported. Gisolf<sup>1</sup> has investigated the ZnS-CdS system, Johnson and Christian,<sup>2</sup> the Ge-Si system, and Folberth,<sup>3</sup> Group III-Group V materials. The results seemed to confirm a postulate that intermediate members of a two-component series have band-gap energies intermediate to those of the extreme members of the series. The present work reports results which show that although the systems ZnS-ZnSe follows the above postulate, the systems ZnS-ZnTe and ZnSe-ZnTe do not.

### EXPERIMENTAL

#### Synthesis of Materials

Phosphor-grade zinc chalcogenides were used throughout the work. Powder mixtures of the pure ingredients

(in the desired molar proportions) were dry ball-milled for six hours, to insure homogeneity of mixing. The materials were then transferred to silica boats, and crystallized in an atmosphere of purified nitrogen at 900°C. The materials were cooled under nitrogen. Phosphor-type purity and precautions were maintained throughout the synthesis.

#### Analysis

X-ray diffraction studies were carried out using a North American Philips diffractometer, with a copper target and nickel filter, to obtain monochromatic 1.54 Å radiation.

Chemical quantitative analyses of tellurium in solid solution were carried out by an electrometric titration method developed by Dr. M. C. Gardels of these laboratories.<sup>4</sup>

#### Reflection Spectra

In the absence of single crystals for direct absorption measurements, the diffuse reflectance of the micro-

<sup>1</sup> J. H. Gisolf, *Physica* **6**, 84 (1939).

<sup>2</sup> E. R. Johnson and S. M. Christian, *Phys. Rev.* **95**, 560 (1954).

<sup>3</sup> O. G. Folberth, *Z. Naturforsch.* **10a**, 502 (1955).

<sup>4</sup> Method to be published elsewhere.

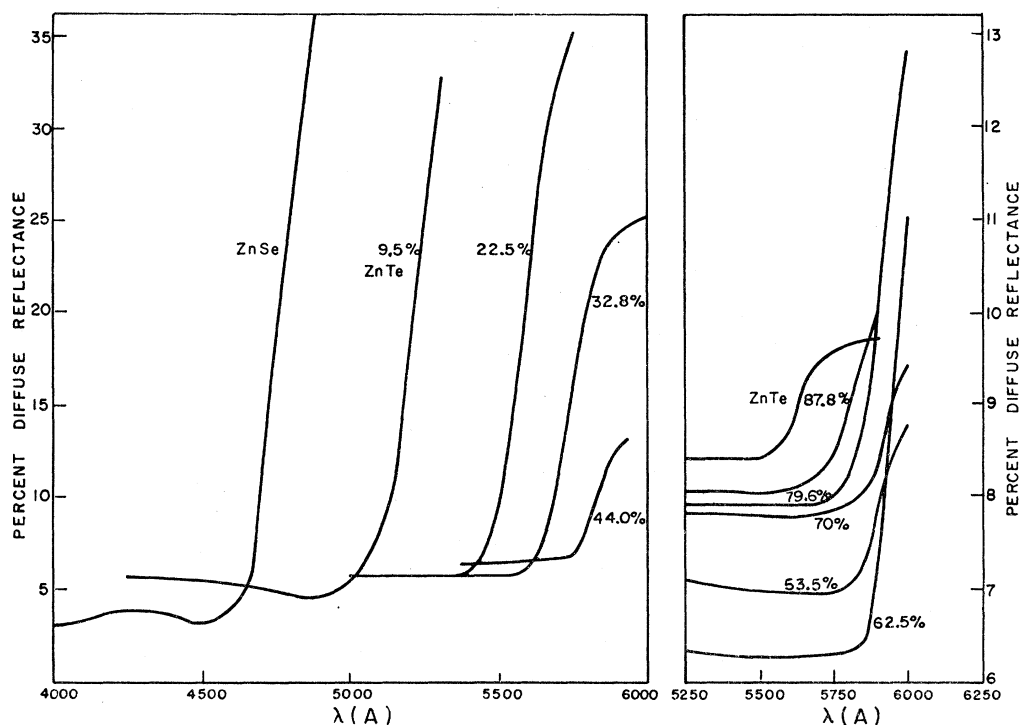


FIG. 1. Diffuse reflectance spectra of zinc seleno-tellurides. Figures indicate mole-percent zinc telluride.

crystalline powders was used to furnish a relative measure of the absorption. Light from either a xenon pressure-arc or a tungsten-filament lamp was passed through a 500 mm Bausch & Lomb monochromator, equipped with an automatic scanning control. The intensity of the diffusely reflected light from approximately 1 cm<sup>2</sup> of the specimen was measured with a 1P21 multiplier phototube. The intensity relative to that from a pressed disk of magnesium carbonate was plotted against wavelength. Values of the energy gap were calculated from the wavelength corresponding to the intersection of the straight-line extrapolation above and below the short-wavelength knee of the curve. Figure 1 shows the diffuse reflectance spectra for several zinc seleno-telluride solid solutions.

### Diffuse Transmission

Measurements of diffuse transmission were made on several materials with a Cary recording spectrophotometer, Model 14. Small amounts of the materials to be tested were ground with KBr (Harshaw, IR Quality) and pressed into translucent pellets. Energy-gap determinations were made by extrapolations on the recorded curves of optical density (log transmission).

### RESULTS AND DISCUSSION

A plot of band gap as a function of composition for the three systems studied is given in Fig. 2. It is seen that a linear variation of band gap with composition

occurs for the system ZnS-ZnSe [Fig. 2(A)]. Figure 2(B) is a similar plot for ZnS-ZnTe. Solid solution in this system occurs only to the extent of about eight mole percent of ZnTe in ZnS, and about five mole percent of ZnS in ZnTe.<sup>5</sup> Figure 2(C) shows a like plot for ZnSe-ZnTe solid solutions. Measurement of the energy gap in this system by diffuse reflection and by diffuse transmission indicate a minimum near a composition of 63 mole percent ZnTe, without exhibiting a discontinuity of slope. A small systematic difference between the reflection and transmission values is attributed to the fact that diffuse reflectance and optical density do not have a simple relationship, so that extrapolations of the type described do not yield completely identical results. The trend, however, is unmistakable.

TABLE I. Band-gap types.

Type of variation	System	Reference
Linear	ZnS-CdS <sup>a</sup>	1
	InAs-InP	3
	ZnS-ZnSe	This work
Discontinuous slope or monotonic convex	Ge-Si	2
Monotonic convex	GaAs-GaP	3
Nonmonotonic concave	ZnS-ZnTe	This work
	ZnSe-ZnTe	

<sup>a</sup> A possible discrepancy in the band-gap value assigned to ZnS by Gisolf, makes it uncertain whether ZnS-CdS should be described as linear or monotonic concave.

<sup>5</sup> Larach, McCarroll, and Shrader, *J. Phys. Chem.* **60**, 604 (1956).

As seen from Fig. 2(C), the variation of band gap with composition for ZnSe-ZnTe, compared with that for Ge-Si, (1) is not linear, (2) is not monotonic, (3) does not have an abrupt change of slope, and (4) is concave. These features suggest that a band scheme other than that suggested by Herman<sup>6</sup> to account for the Ge-Si anomaly, should be sought. In particular, it would appear that some specific property peculiar to the Te

TABLE II. Room temperature band-gap energies.

Material	Band gap (ev)	Method	Reference
Cub.-ZnS	3.64	Absorption	a
	3.60	Luminescence	b
	3.60	Reflectivity	This work
Cub.-ZnSe	2.58	Photoconductivity	c
	2.66	Luminescence	b
	2.66	Reflectivity	This work
Cub.-ZnTe	2.64	Transmission	This work
	2.15	Absorption	c
	2.10	Photoconductivity	d
	2.22	Reflectivity	This work
	2.26	Transmission	This work

<sup>a</sup> F. A. Kroger and J. E. Hellingman, J. Electrochem. Soc. **93**, 156 (1948).

<sup>b</sup> R. E. Shrader (unpublished data).

<sup>c</sup> H. B. DeVore (unpublished data).

<sup>d</sup> R. H. Bube and E. L. Lind, Phys. Rev. **105**, 1711 (1957).

TABLE III. Lattice spacings of ZnSe-ZnTe.

Initial composition	Analyzed ZnTe fraction	Lattice spacing (Å)
ZnSe	...	5.6684
0.9 ZnSe:0.1 ZnTe	...	5.705
0.8 ZnSe:0.2 ZnTe	0.226	5.761
0.7 ZnSe:0.3 ZnTe	0.328	5.811
0.6 ZnSe:0.4 ZnTe	0.440	5.857
0.5 ZnSe:0.5 ZnTe	0.535	5.899
0.4 ZnSe:0.6 ZnTe	0.633	5.940
0.3 ZnSe:0.7 ZnTe	0.700	5.977
0.2 ZnSe:0.8 ZnTe	0.793	6.022
0.1 ZnSe:0.9 ZnTe	0.875	6.055
ZnTe	...	6.100

atom (or ion) may bear directly on the behavior of solid solutions containing Te.

Comparison of the exact nature of the dependence of band gap on composition suggests that each dependence may be categorized in one or more ways, as for example, linear, nonlinear but monotonic-concave (or -convex, etc.). Table I summarizes in this manner some available data on band-gap dependence.

<sup>6</sup> F. Herman, Phys. Rev. **95**, 847 (1954).

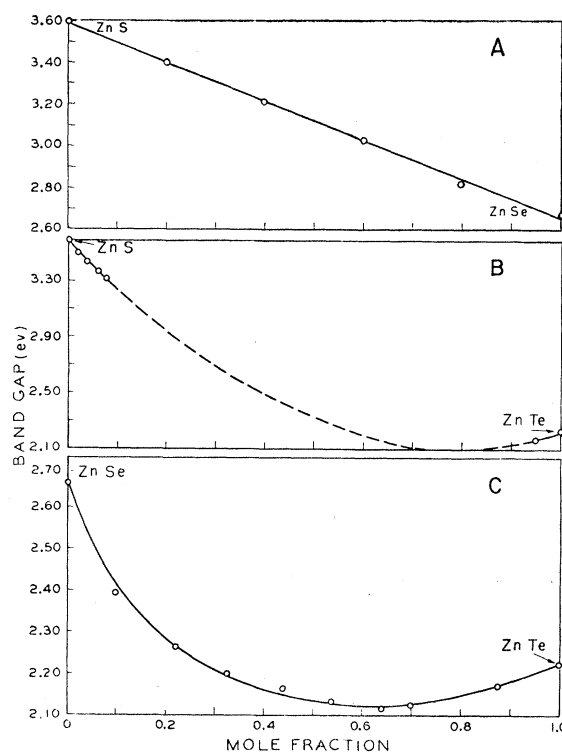


Fig. 2. Band gap as a function of composition for (A) zinc sulfo-selenides; (B) zinc sulfo-tellurides; (C) zinc seleno-tellurides.

### Band-Gap Determinations

Several methods exist for the measurement of band gaps in solids. These include: absorption, transmission, reflectance, photoconductivity, and luminescence. Table II lists and compares the band gaps obtained by the various methods with those obtained in this work.

### Lattice Spacings

The lattice spacings of solid solutions of ZnSe and ZnTe follow Vegard's law throughout the range. Table III lists the initial composition prior to crystallization, the analyzed amount of ZnTe after crystallization, and the lattice spacing of the solid solution.

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