

Investigations of the thermodynamic properties of zinc chalcogenides

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Abstract

The standard free energies of formation of zinc chalcogenides (ZnTe, ZnSe and α -ZnS) have been determined by an electrochemical technique using LiCl–KCl + 5 wt.% ZnCl₂ electrolyte. The standard enthalpies of formation of ZnTe and ZnSe, and the enthalpy of fusion of ZnTe have been measured directly in a DTA calorimeter. Good agreement has been observed between the enthalpies of formation obtained by these two independent techniques. The thermodynamic behaviour of these compounds at their melting point has been discussed by using the enthalpy of fusion of ZnSe and ZnS reported in the literature and that of ZnTe determined in this investigation.

The lattice constants of these compounds have been calculated from the tetrahedral covalent, ionic and rationalised (after Phillips) radii of the component elements, and compared with those determined by X-ray diffraction technique. The estimated values of the enthalpy of formation (based on Pauling's and Phillips' methods) and the standard entropy (based on Latimer's method) have been compared with the experimental values and discussed in the light of the structure and bonding of the compounds. Detailed analyses of the thermodynamic and structural data reveal that the bonding in zinc chalcogenides is neither predominantly covalent nor ionic.

INTRODUCTION

There is only one stoichiometric compound with equiatomic composition in each of the systems, Zn–Te, Zn–Se and Zn–S [1]. These compounds belong to the family of broad band gap semiconductors and have gained prominence for their applications in various electronic devices [2,3], such as light-emitting diodes (L.E.D.), photovoltaic detectors, electroluminescence, vacuum fluorescent tubes, optical wave guides, modulators, lasers, etc. Most research on these chalcogenides is concerned with their physical and electronic properties; their thermodynamic properties have not been sys-

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tematically investigated. The available thermodynamic data show wide disagreements, inconsistencies and error limits. Because the knowledge of accurate and reliable thermodynamic data is of considerable importance for the growth of semiconducting crystals and for an understanding of their intrinsic stability towards changing environments, it was considered worthwhile to determine accurately the thermodynamic properties of zinc chalcogenides by two independent methods, namely, an electrochemical technique and calorimetry.

The present authors have recently published some thermodynamic properties of ZnTe [4] and ZnSe [5]. In this paper, a systematic study of the thermodynamic properties of ZnTe, ZnSe and α -ZnS is reported. The results have been compared with the available data and also with those calculated theoretically, and are discussed in terms of the structure and bonding of the compounds.

EXPERIMENTAL

Materials

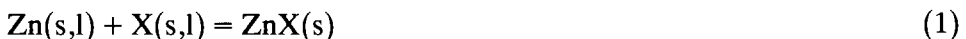
High purity zinc, tellurium, selenium, sulphur and copper (each 99.999% pure) and antimony (99.99% pure), obtained from Johnson Matthey (UK) and the Bhabha Atomic Research Centre (India), respectively, were used in this investigation. The following Analytical Reagent grade salts were used for preparation of the electrolyte: zinc chloride (Loba-Chemie, India), lithium chloride (Sisco, India) and potassium chloride (Qualigens, India).

Preparation of compounds

The compounds ZnTe, ZnSe and α -ZnS were prepared by pyrosynthesis from the constituent elements. The specific elements were weighed in stoichiometric proportions to an accuracy of 10^{-5} g and sealed in transparent quartz capsules under a vacuum of better than 10^{-5} Torr. The capsules were heated at a rate of 2.5 K min^{-1} to 1300 K and held at this temperature for about 40 h, then at 1420 K for about 5 h, and finally quenched in cold water.

Electrochemical measurements

The standard free energies of formation of zinc chalcogenides were determined by measuring the open circuit e.m.f. of the galvanic cell $\text{Zn(s,l)}|\text{LiCl-KCl} + (5 \text{ wt.}\%) \text{ZnCl}_2|\text{ZnX(s)} + \text{X(s,l)}$ where X represents Te, Se or S. The virtual cell reaction is



The standard free energy of formation was calculated from the relation

$$\Delta G^{\ominus} = -nFE \quad (2)$$

where n is the number of electrons transferred during reaction (1), E is the open circuit e.m.f. of the cell and F is the Faraday constant.

A cell assembly made of borosil glass containing two lower limbs (8 mm internal diameter) below a tubular electrolyte compartment (35 mm internal diameter) was used in this investigation. At the bottom of each limb was sealed a tungsten lead wire, 0.4 mm in diameter and 20 cm in length. The compounds ZnTe, ZnSe or α -ZnS, with 10 at.% excess tellurium, 15 at.% excess selenium or 20 at.% excess sulphur, respectively, were formed in one limb by heating under argon (up to 700, 650 or 600 K, respectively) a homogeneous mixture of the powders of the respective chalcogenide and chalcogen element. In the other limb, 6 g of pure zinc was melted under argon. The details of the experimental technique and cell assembly have been described elsewhere [6,7].

The cell temperature and e.m.f. were both measured by a Digital Electrometer (Keithley, USA; Model 617) at an input impedance of greater than $2 \times 10^{12} \Omega$. The cell attained equilibrium after 24 h and thereafter the e.m.f. values remained stable for over 30 h. The e.m.f. measurements were made during both heating and cooling cycles and were reproducible within ± 1 –2 mV. In each case three independent runs were performed to check the reproducibility of the results.

Differential thermal analysis calorimetry

The standard enthalpies of formation of ZnTe and ZnSe, and the enthalpy of fusion of ZnTe were measured directly in a quantitative differential thermal analysis (DTA) calorimeter using a stainless steel block as a reference surrounding. The calorimeter has been successfully employed for the study of a number of chalcogenides, namely CdTe [7], CdSe [8] and CdS [9]. The construction and operation of the calorimeter were similar to those described by Shamsuddin and coworkers [7,10].

A thorough mixture (7.26125 g for ZnTe and 2.21565 g for ZnSe) of fresh powders of zinc ($-150 \mu\text{m}$) and tellurium or selenium ($-100 \mu\text{m}$) in stoichiometric proportion corresponding to the composition ZnTe or ZnSe, respectively, was taken in the graphite sample container of the calorimeter, which after evacuation and insertion of argon (with oxygen impurity less than 2 ppm) was heated at a constant and reproducible rate of 4 K min^{-1} by a Thermal Program Controller (ULVAC, Sinku-Riku, Japan; Model, HPC-7000). The temperature of the sample and the differential temperature ΔT between the sample and the reference block were recorded with a four-pen recorder (BBC, Austria; Model, SE-460). During the exothermic pyrosynthesis of the compound, values of ΔT showed a pronounced up-

ward peak, from the area of which the enthalpies of formation were obtained. For the calculation of the enthalpy of formation of ZnTe, the calorimeter was calibrated by studying the fusion of pure tellurium and antimony under conditions identical with those of the runs with the powder mixture of zinc and tellurium. The calibration for ZnSe was performed by studying the fusion of zinc, antimony and selenium. The mean calibration coefficient was employed to calculate the enthalpies of formation of ZnTe and ZnSe. The endothermic calibration for the exothermic reactions was checked by determining the standard enthalpy of formation of SnTe (the enthalpy of formation of SnTe is well established and known accurately).

In the DTA calorimeter, even after the ZnTe compound formation reaction was complete, the product continued to be heated beyond the melting temperature of ZnTe. A sharp endothermic peak was observed during the fusion of ZnTe. The enthalpy of fusion of ZnTe was calculated from the area of this peak. For this purpose the calorimeter was calibrated by studying the fusion of pure copper.

In each case three independent runs were carried out to check the reproducibility of the results.

RESULTS AND DISCUSSION

Free energies of formation

Table 1 lists the E versus T equations, obtained by the least-squares method from the e.m.f. values measured at different temperatures, for the galvanic cells employed for the study of ZnTe, ZnSe and α -ZnS. Based on these equations, the ΔG^\ominus versus T relationships for the different reac-

TABLE 1
 E versus T relationships for different galvanic cells

$E = A + BT$ (mV)		Error limit (mV)	Temperature range (K)
A	$-B$		
$\text{Zn(s,l)} \text{LiCl-KCl} + (5 \text{ wt.}\%)\text{ZnCl}_2 \text{ZnTe(s)} + \text{Te(s,l)}$			
618.4	0.0642	1.0	640–693
657.3	0.1201	1.0	693–723
751.8	0.2508	1.0	723–845
$\text{Zn(s,l)} \text{LiCl-KCl} + (5 \text{ wt.}\%)\text{ZnCl}_2 \text{ZnSe(s)} + \text{Se(l)}$			
962.2	0.1467	1.9	640–693
997.8	0.1980	1.8	693–825
$\text{Zn(s)} \text{LiCl-KCl} + (5 \text{ wt.}\%)\text{ZnCl}_2 \alpha\text{-ZnS(s)} + \text{S(l)}$			
1088.6	0.1435	2.1	640–690

TABLE 2

 ΔG^\ominus versus T relationships for formation of zinc chalcogenides from different sources

Reaction	ΔG^\ominus (J mol ⁻¹)	
	Present investigation	Literature
Zn(s) + Te(s) = ZnTe(s)	(-119360 + 12.39T) ± 200 (640 < T < 693 K)	(-117642 + 11.00T) [12]
Zn(l) + Te(s) = ZnTe(s)	(-126870 + 23.18T) ± 200 (693 < T < 723 K)	-
Zn(l) + Te(l) = ZnTe(s)	(-145110 + 48.41T) ± 200 (723 < T < 845 K)	(-147400 ± 53.62T) [20]
Zn(s) + Se(l) = ZnSe(s)	(-185720 + 28.31T) ± 370 (640 < T < 693 K)	-
Zn(l) + Se(l) = ZnSe(s)	(-192590 + 38.22T) ± 350 (693 < T < 825 K)	(-179430 + 45.514T) [20]
Zn(s) + S(l) = α -ZnS(s)	(-210117 + 27.70T) ± 410 (640 < T < 690 K)	-

tions associated with the formation of zinc chalcogenides have been established and are presented in Table 2. The free energy of formation of ZnTe has been determined by McAteer and Seltz [11], Zabdyr [12] and Fleming and Stevenson [13] by electrochemical technique. All these investigators studied only the equilibrium between solid zinc and solid tellurium. In the low temperature range (640–693 K), our result is comparable with the ΔG^\ominus versus T expression reported by Zabdyr [12] (listed in Table 2).

Employing an electrochemical technique, Terpilowski and Ratajczak [14] have measured the free energy of formation of ZnSe in the very narrow temperature range of 360–420 K, whereas Newns [15] conducted studies at only one temperature, 643 K. The value $\Delta G_{643\text{ K}}^\ominus = -167.5$ kJ mol⁻¹, based on our equation (Table 2), is in excellent agreement with the value of -166.4 kJ mol⁻¹ obtained by Newns [15].

The free energy of formation of α -ZnS has been determined by a number of investigators using chemical equilibrium [16], vapour pressure [17] and electrochemical [18,19] techniques. All the investigators performed high-temperature measurements (above 948 K) and, surprisingly, so far no attempt has been made to measure its thermodynamic properties below 948 K. Hence no experimental data on α -ZnS in the lower temperature range is available for comparison.

Making use of the available thermodynamic and phase equilibria data and the 'associated solution model' for the liquid phases in the binary systems Zn–Te, Zn–Se and Zn–S, and considering the ZnTe, ZnSe and ZnS phases as line compounds, Sharma and Chang [20] have established the ΔG^\ominus versus T relationships for the formation of zinc chalcogenides. For comparison, these relationships are also incorporated in Table 2. Table 2 shows that our ΔG^\ominus versus T equation for the reaction Zn(l) + Te(l) =

TABLE 3

Standard free energies of formation of zinc chalcogenides at 298 K from different sources

Compound	$-\Delta G^\ominus$ (kJ mol ⁻¹)			
	Present investigation	Literature		
		Value	Ref.	Method
ZnTe	115.2 ± 1.0	114.5	11	Electrochemical
		113.9 ^a	12	Electrochemical
		110.5 ± 3.8	13	Electrochemical coulometric titration
ZnSe	173.6 ± 1.5	159.0 ± 2.1	14	Electrochemical
		166.4 ^b	15	Electrochemical
α -ZnS	200.0 ± 2.0	-	-	-

^a Estimated value.^b Value at 643 K.

ZnTe(s) is in excellent agreement with that obtained by Sharma and Chang. However, our result is not comparable with the ΔG^\ominus versus T relationship reported by Sharma and Chang for the reaction $\text{Zn(l)} + \text{Se(l)} = \text{ZnSe(s)}$. This discrepancy may be due to the error involved in the thermodynamic and phase equilibria data used by Sharma and Chang.

The free energies of formation of zinc chalcogenides at 298 K have been calculated from the ΔG^\ominus versus T relationships by taking into account the enthalpies of fusion of zinc and chalcogen elements and Kirchhoff's law correction [1,21]; these are listed in Table 3 together with the available literature data. Our results are in reasonable agreement with those reported in the literature.

Table 2 clearly indicates that the negative values of free energy of formation of all the compounds decrease with increasing temperature. Thus, the thermodynamic stability of these compounds decreases with increasing temperature. Furthermore, Tables 2 and 3 suggest that under similar conditions the stability of these chalcogenides increases in the following order: $\text{ZnTe} < \text{ZnSe} < \alpha\text{-ZnS}$.

Enthalpies of formation

The enthalpies of formation of ZnTe and ZnSe at 812 K and 707 K obtained by DTA calorimetry are -146.1 ± 1.2 and -193.0 ± 1.5 kJ mol⁻¹, respectively. These values of enthalpy of formation are in excellent agreement with the respective average values of -145.1 ± 1.3 (in the temperature range 723–845 K) and -192.6 ± 2.2 kJ mol⁻¹ (in the temperature range 693–825 K) obtained by electrochemical measurements (Table 2). The standard enthalpies of formation of ZnTe and ZnSe at 298 K have been calculated by taking into account the enthalpies of fusion of zinc and

TABLE 4

Standard enthalpies of formation of zinc chalcogenides at 298 K from different sources

Compound	$-\Delta H^\ominus$ (kJ mol ⁻¹)					
	Present investigation			Literature		
	Electro-chemical	DTA calorimetry	Proposed value	Value	Ref.	Method
ZnTe	118.0	119.0 ± 2.0	119.0 ± 2.0	119.2 ± 0.4	1	Compilation
				118.0	11	Electrochemical
				116.6 ± 0.6	12	Electrochemical
				119.2 ^a	22	Liquid metal solution calorimetry
ZnSe	177.2	177.6 ± 2.5	177.6 ± 2.5	159.0 ± 8.4	1	Compilation
				163.2 ± 2.9	14	Electrochemical
				177.0	15	Electrochemical
α -ZnS	204.6	-	204.6	205.0 ± 2.1	1	Compilation
				194.0 ± 0.5	17	Vapour pressure
				204.1	18	Electrochemical
				203.3	19	Electrochemical

^a Value at 273 K.

tellurium (selenium) and Kirchhoff's law correction. The values at 298 K are in very good agreement with those extrapolated from the ΔG^\ominus versus T equations. The value of $\Delta H_{298\text{ K}}^\ominus$ for α -ZnS has been estimated from the electrochemical data (Table 2, $\Delta H_{640-690\text{ K}}^\ominus = -210.1$ kJ mol⁻¹). The resulting values of the standard enthalpy of formation of ZnTe, ZnSe and α -ZnS at 298 K are summarised in Table 4. The values of the standard enthalpy of formation of zinc chalcogenides determined by other investigators are also included in the table for comparison. Table 4 shows that our value of $\Delta H_{\text{ZnTe}}^\ominus$ is in excellent agreement with that measured directly by Pool [22] using liquid metal solution calorimetry.

Entropies of formation

The entropy of formation of a compound can best be calculated from a combination of the experimental values of the enthalpy of formation and the free energy of formation using the equation

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus \quad (3)$$

The values of ΔS_{298}^\ominus thus obtained for ZnTe, ZnSe and α -ZnS are -12.8, -13.4 and -15.3 J K⁻¹ mol⁻¹. The large negative values of the entropy of formation suggest that the vibrational entropy term plays a predominant role in the formation of the compounds. Moreover, the negative values of entropy of formation are consistent with the well-ordered tetrahedral

TABLE 5

Standard entropies of zinc chalcogenides at 298 K from different sources

Compound	S^\ominus (J K ⁻¹ mol ⁻¹)			
	This investigation	Literature		
		Value	Ref.	Method
ZnTe	78.4	77.8	1	Compilation
		82.3	12	Electrochemical
ZnSe	70.5	70.3	1	Compilation
α -ZnS	58.2	57.7	1	Compilation

structure of ZnTe, ZnSe and α -ZnS, and the presence of the strong bonds of Zn–Te, Zn–Se and Zn–S, respectively.

The standard entropies of zinc chalcogenides at 298 K obtained from the values of the entropy of formation are in reasonable agreement with those reported in the literature (Table 5).

Enthalpies and entropies of fusion

The enthalpy of fusion of ZnTe ΔH_{ZnTe}^f obtained in this investigation is 63.0 ± 2.5 kJ mol⁻¹, which is in good agreement with the value of 64.7 kJ mol⁻¹ determined calorimetrically by Kulwicki [23] and also with the value of 63.9 kJ mol⁻¹ estimated by Sharma and Chang [20]. Another value of 57.7 kJ mol⁻¹ reported by Vignodovich et al. [24] is less endothermic.

Because it was not possible to measure the enthalpies of fusion of ZnSe and ZnS in our DTA calorimeter because of their very high melting points and sublimation prior to melting and as such no experimental values have been reported, the values of 51.9 and 59.7 kJ mol⁻¹ for the enthalpies of fusion of ZnSe and ZnS, respectively, optimised by Sharma and Chang [20], have been adopted for analysis.

The values of the entropy of fusion of ZnTe, ZnSe and ZnS, as calculated by the expression

$$\Delta S_{\text{ZnX}}^f = \frac{\Delta H_{\text{ZnX}}^f}{T_{\text{ZnX}}^f} \quad (4)$$

are given in Table 6. The theoretical values of the entropy of fusion of zinc chalcogenides may be estimated according to the procedure outlined by Kubaschewski and Alcock [21] by adding the entropies of fusion of the component elements to their entropy of mixing. Because experimental values for the entropy of mixing of zinc and chalcogen elements are not available, complete order in the solid and complete disorder in the liquid

TABLE 6

Entropies of fusion of zinc chalcogenides

Compound	ΔS^f (J K ⁻¹ mol ⁻¹)	
	Experimental/ literature [20]	Theoretical
ZnTe	40.1 ± 1.6	46.3
ZnSe	28.8	33.9
ZnS	30.0	26.3

state may be assumed. The theoretical value of the entropy of fusion of ZnX is thus given by

$$\Delta S_{ZnX}^f = \Delta S_{Zn}^f + \Delta S_X^f - 4R (0.5 \ln 0.5) \quad \text{J K}^{-1} \text{ mol}^{-1} \quad (5)$$

The values obtained from eqn. (5) are also incorporated in Table 6. Table 6 clearly indicates that theoretical values for ZnTe (and ZnSe) are larger than those obtained by us (and by Sharma and Chang [20]). This indicates that full entropy is not generated during melting, that molten ZnTe and ZnSe may not be completely disordered and that the solid ZnTe (and ZnSe) may not be perfectly ordered at their melting point. Also, some amount of non-configurational entropy may be involved. Contrary to this, the theoretical value of the entropy of fusion of ZnS is smaller than that based on the data of Sharma and Chang [20]. This discrepancy may be due to error involved in the thermodynamic and phase equilibria data used by Sharma and Chang in their calculation. In addition, it may be attributed to (i) neglecting the vibrational contribution of the entropy of fusion and (ii) the highly non-metallic character of sulphur, introducing a term in the entropy for the hypothetical transformation of sulphur to its metallic form.

Structure and bonding

All the compounds, ZnTe, ZnSe and α -ZnS, crystallise in the zinc blende cubic structure. The experimental values of cubic lattice parameter

TABLE 7

Experimental and theoretical lattice constants (Å) of zinc chalcogenides

Compound	Experimental		Theoretical					
	<i>a</i>	<i>l</i>	Covalent radii		Rationalised radii		Ionic radii	
			<i>a</i>	<i>l</i>	<i>a</i>	<i>l</i>	<i>a</i>	<i>l</i>
ZnTe	6.069	2.63	6.074	2.63	6.074	2.63	6.489	2.81
ZnSe	5.667	2.45	5.658	2.45	5.658	2.45	5.958	2.58
α -ZnS	5.426	2.35	5.427	2.35	5.432	2.35	5.672	2.42

a and bond length l of zinc chalcogenides, determined in this investigation by X-ray diffractometry, are listed in Table 7. The theoretical values of the lattice constants based on the tetrahedral covalent [25], ionic [26] and rationalised (after Phillips [27]) radii of zinc and chalcogen atoms, as estimated by the relationship [28]

$$r_{\text{Zn}} + r_{\text{X}} = l_{\text{ZnX}} = a(\sqrt{3}/4) \quad (6)$$

are also incorporated in the table. Table 7 clearly indicates that the experimental values of the lattice constants are in good agreement with those calculated from the covalent and rationalised component radii of the compounds. The wide disagreement between the estimated lattice constants based on the ionic radii and the experimental values reflects the non-ionic nature of these compounds.

Pauling [25] has presented the following empirical equation for the calculation of the standard enthalpy of formation of an ionic compound, AB

$$\Delta H_{\text{AB}}^{\ominus} = -193\,016(X_{\text{A}} - X_{\text{B}})^2 \quad \text{J mol}^{-1} \quad (7)$$

where X refers to the value of electronegativity. The enthalpies of formation of zinc chalcogenides as obtained by substituting the electronegativity values from the scale due to Pauling [25] in the above equation are compared with the experimentally determined values in Table 8. There is wide disagreement between the experimental values of the enthalpies of formation and those estimated from Pauling's equation. This disagreement suggests that Pauling's formulation may not be applicable in these chalcogenides. This discrepancy may be due to the partial ionic character of the bonds in these compounds.

Phillips [27] has improved the empirical formula for the calculation of the enthalpy of formation, by considering both the ionicity and metallisation terms, based on the spectroscopic data. The enthalpies of formation of zinc chalcogenides as obtained from Phillips' method, are also incorporated

TABLE 8

Experimental and empirical values of standard enthalpies of formation of zinc chalcogenides at 298 K

Compound	$-\Delta H^{\ominus}$ (kJ mol ⁻¹)		
	Experimental	Empirical	
		Pauling (ionic)	Phillips (spectroscopic)
ZnTe	119.0	48.3	108.4
ZnSe	177.6	123.5	166.5
α -ZnS	204.6	156.3	176.1

TABLE 9

Experimental and theoretical values of standard entropies of zinc chalcogenides at 298 K

Compound	S^\ominus (J K ⁻¹ mol ⁻¹)	
	Experimental	Theoretical (Latimer)
ZnTe	78.4	96.2
ZnSe	70.5	93.3
α -ZnS	58.2	66.5

in Table 8. It is observed that the values predicted by Phillips' spectroscopic formulation are in remarkably good agreement with those measured experimentally.

Latimer [29] has proposed a method for calculation of the standard entropy of an ionic compound by adding the entropies of the constituent cationic and anionic elements. The standard entropies of zinc chalcogenides, estimated by assuming the presence of zinc as a bivalent cation and the chalcogens (Te, Se and S) as bivalent anions, are listed in Table 9 together with those based on the experimental data. This table clearly indicates that the values of the standard entropy due to Latimer are considerably higher than those based on the experimental data. Thus analysis of the standard entropy also reflects the insignificant ionic nature of the bonding in these compounds. The ionicity of the bonds in zinc chalcogenides, estimated quantitatively from Pauling's equation [25]

$$\text{Ionicity} = 1 - \exp(-0.25(X_A - X_B)^2) \quad (8)$$

is summarised in Table 10. The corresponding values of ionicity based on the band theory of Phillips [27] are also incorporated in the table. From the table it is clear that the values of the ionicity of the bonds in these compounds based on two independent methods differ widely. The Pauling values are much lower than the Phillips values. Pauling's ionicity values, however, show a systematic variation and a decreasing trend is observed with increasing anion size from S to Te. This is not consistent with the

TABLE 10

Ionicity values of zinc chalcogenides

Compound	Ionicity	
	Pauling	Phillips
ZnTe	0.06	0.609
ZnSe	0.15	0.630
ZnS	0.18	0.623

accepted hypothesis of increasing ionicity with the increasing ionic size of elements of the same group of the periodic table because of their decreasing ionic potentials. Phillips' ionicity values, however, show a random variation. Obviously neither Pauling's formulation nor Phillips' formulation gives correct ionicity values.

In the light of the above discussions, one may conclude that bonding in zinc chalcogenides is neither substantially ionic nor covalent.

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