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Hf(Se_xTe_{1-x})₂: Deviation from Végard's Law in Mixed Systems

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Polycrystalline Hf(Se_xTe_{1-x})₂ has been prepared by iodine mineralization from the elements at 800 °C. Homogeneous solid solutions result over the range 0 < x < 1. Hexagonal *a* and *c* parameters, determined by using the Debye-Scherrer method, were found to vary linearly and parabolically, respectively, with composition. The non-Végard behavior is ascribed to packing mismatches in the layers and is compared to behavior in other mixed transition-metal dichalcogenides. A brief comparison to pyrite systems is presented, and some general aspects of mixed materials are discussed.

Introduction

The layered transition-metal dichalcogenides exhibit a diversity of properties. Conductivities range from insulating HfS₂ with a 2-eV band gap^{1c} to good metals; many are superconducting. Intercalation by amines and alkali metals, charge density waves,² and unusual lubricating properties can all be attributed to the layered structure. Nonstoichiometry corresponding to an anion/cation ratio of less than 2 is the general rule for these materials. Whereas studies of superconductivity, metal-insulator transitions, and unusual magnetic properties are of basic interest, applications include battery and electrode materials such as Li₂TiS₂³ and broad range catalysts, for example, cobalt-doped MoS₂.

The structural similarity of the layered dichalcogenides allows a large number of mixed materials to be synthesized over the entire range of solubility, i.e., 0 < x < 1 for M_xM'_{1-x}Ch₂ and M(Ch'_xCH''_{1-x})₂. (Ch stands for chalcogen.) This not only provides new materials with new properties at intermediate composition but also allows the study of composition-dependent behavior such as the metal-insulator transition in Hf(Se_xTe_{1-x})₂.^{4,5} In addition, mixed systems can provide information that complements results found for the pure material. As an example, Hf(Se_xTe_{1-x})₂ was used to determine the basis for the metallic conductivity of HfTe₂.⁵

Végard's law predicts for solid solutions a linear dependence of lattice parameter on composition. A breakdown of the assumptions of Végard's law in the mixed-anion layered materials provides a means to study their structure. Measures of ion sizes and layer spacing are qualitatively discussed below. The magnitude of the deviation from linearity can also provide insights into the different electronic structures of insulators and metals and the choice of layered and pyrite structure in dichalcogenides.

In this paper we report the synthetic methods and lattice parameters for Hf(Se_xTe_{1-x})₂. Deviations from Végard's law in this system are compared to those in other mixed layered materials. A comprehensive list of such systems is presented with a general quantitative description, and several qualitative trends are discussed. A brief comparison of the behavior of pyrites and dichalcogenides completes the presentation.

Experimental Section

Hf(Se_xTe_{1-x})₂ samples were prepared by reacting stoichiometric amounts of 99.7% hafnium powder (from Alfa), 99.99% selenium shot (from Atomergic), and 99.999% tellurium chunks (from Alfa). The materials were shown to be oxygen free and were handled under helium in a controlled environment chamber (Dri-lab) where the oxygen

Table I. Lattice Parameters for Hf(Se_xTe_{1-x})₂

<i>x</i> ± 0.02	<i>c</i> ± 0.008 Å	<i>a</i> ± 0.008 Å	<i>x</i> ± 0.02	<i>c</i> ± 0.008 Å	<i>a</i> ± 0.003 Å
0.000	6.658	3.951	0.650	6.441	3.821
0.100	6.649	3.939	0.667	6.432	3.817
0.150	6.635	3.927	0.700	6.405	3.807
0.200	6.629	3.919	0.750	6.362	3.794
0.275	6.607	3.900	0.800	6.330	3.785
0.333	6.575	3.886	0.800	6.330	3.787
0.350	6.585	3.881	0.875	6.288	3.775
0.425	6.550	3.868	0.850	6.293	3.777
0.500	6.521	3.852	0.875	6.267	3.768
0.500	6.514	3.850	0.900	6.243	3.764
0.500	6.520	3.853	0.925	6.227	3.762
0.600	6.464	3.828	1.000	6.154	3.746
0.625	6.450	3.825			

content and the nitrogen content were kept below 1 ppm. The elements were loaded into outgassed quartz tubes with iodine (~5 mg/cm³ of reaction volume). The samples were pumped for 15 min at ~10⁻⁶ torr, with a liquid nitrogen trap. Iodine sublimed into the trap was sublimed back into the reaction vessel, which was then sealed. Mineralization was chosen over a transport process as it was felt that this would give more homogeneous crystals. The tubes were put in flat furnaces at 600 °C for 1 week and then at 800 °C for 2, 3, or 4 weeks. The temperature 800 °C was chosen to prevent hafnium tube attack. Growth time depended on the desired crystal size. The crystals produced were hexagonal plates up to 5 × 5 mm² for the end members of the series but decreased to 2 × 2 mm² for *x* values close to *x* = 0.5. Reaction times longer than 4 weeks seemed to have little effect on the crystal size. Compositions shown are nominal, but several were determined directly by heating at 900 °C in an oxygen flow to form HfO₂. In these cases, *x* was found to be within 0.02 of nominal value.

A helium drybox procedure was used for preparing the products for Debye-Scherrer X-ray analysis. All samples were sifted through a <325-mesh screen, loaded into 0.3-mm capillaries, and sealed. The X-ray powder patterns were of excellent quality and free of extra phases (except for an early HfSe₂ preparation). The *a* and *c* lattice parameters as determined from a least-squares fit of the patterns are given in Table I.

The deviation of *c/a* from that expected by Végard's law is given in Figure 1. While HfSe₂ can be prepared very close to stoichiometry,⁶ HfTe₂ is always slightly tellurium deficient.^{4,7-9} Whereas this can greatly affect the electrical properties,^{4,5} it seems to have little effect on the packing mismatch.

Discussion

In the study of alloys, solid solutions, and mixed systems, the determination of crystal-cell dimensions as a function of composition is of primary importance to an understanding of structure and properties. In a two-component system, to a first approximation, Végard's law is obeyed; it is defined as the

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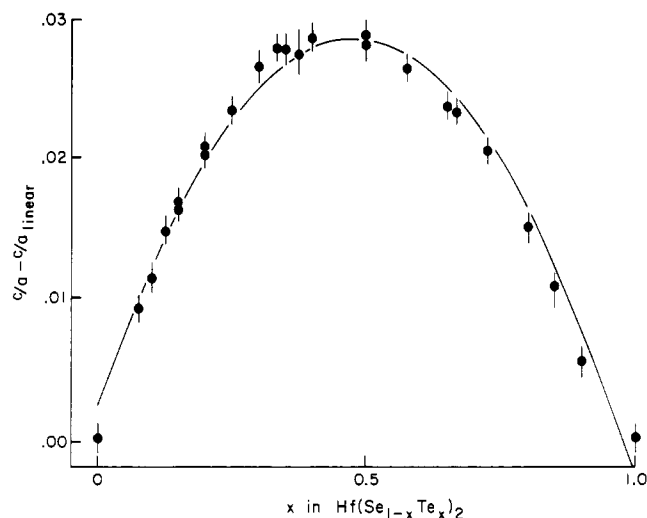


Figure 1. Deviation from linearity of c/a vs. composition in the series $\text{Hf}(\text{Se}_{1-x}\text{Te}_x)_2$.

linear variation of lattice parameters with the mole fraction of one component. Deviations from linearity are often observed but are rarely more than a few percent, and, when larger, insolubility and changes in crystal symmetry may result. Végard's law is best regarded as the first term in a perturbation approach, but physical origins can be stated. At intermediate composition the bond lengths between mixed atoms can be assumed to be the average of the lengths of the corresponding bonds in the pure material. Averaging over pair bonds results in linear variation of bond length, hence lattice constant, with composition (see pair averaging for layered system below and eq 1c and 2a).

The applicability of Végard's law can be expected only in systems where (1) the end members of the series are of the same structure and symmetry and (2) all the corresponding atoms are on special crystallographic sites or, when atoms are on general sites, all the corresponding positions scale. It must be remembered that lattice parameters reflect detailed structure only in part. Linear variation of distances between atoms in general positions need not result in linear variations in lattice parameters. Geometry (or symmetry) restrictions may make impossible the simultaneous linear change of all bond lengths. Therefore, several bonds may vary nonlinearly for geometry reasons, even though the energetically dominant and structure-determining bond varies linearly. If the atomic sizes in the end members of the series are sufficiently different, additional nonlinearity may result from packing mismatches due to core repulsions. At intermediate compositions atoms from the two constituents will be randomly distributed, and (again invoking a linear dependence of some energetically dominant bond) core repulsions become possible between adjacent larger atoms. The lattice may relax in a way that maintains the energy of the dominant bond but reduces core repulsion energy, resulting in a nonlinear dependence of some lattice parameter. Such processes will generally result in positive deviations from Végard's law, whereas geometry restrictions may result in deviations of either sign. It should also be remembered that geometry and packing considerations are not necessarily independent. As discussed below, the lattice behavior of $\text{Hf}(\text{Se}_x\text{Te}_{1-x})_2$ is consistent with packing mismatch.

Layered Materials. The layered transition-metal dichalcogenides can be pictured as hexagonal layers of metal (M) or chalcogen (Ch) atoms stacked to form a Ch-M-Ch sandwich. The metal is six-coordinate and can be of either D_{3h} or D_{3d} symmetry. The sandwiches are then stacked in a variety of ways, with all D_{3d} , all D_{3h} , or mixed D_{3d} and D_{3h} layers. van der Waals forces bond the layers, and the unoc-

Table II. Mixed-Anion Systems

	a^a	c^a	Δc^b	ref	com- ment
TiSSe	3.457	5.868	0.022	15-18	
TiSTe	3.586	6.192	0.083	15	
TiSeTe	3.643	6.291	0.025	15	
ZrSSe	3.715	6.013	0.039	17, 19-21	
ZrSeTe	3.861	6.465	0.089	22	
HfSSe	3.694	6.061	0.055	1, 23, 24	
HfSTe	3.795	6.475	0.2195	4	
HfSeTe	3.851	6.520	0.124	4, 5, this work	
NbSSe				25, 26	c
NbSeTe				27	d
TaSSe	3.384	6.188	0.0025	25, 28-31	e
TaSeTe				32	f
MoSSe	3.222	6.353	0.044	10, 33, 34	
WSSe	3.218	6.374	0.0385	35	
WSTe	3.168	6.227		35	g
WSeTe	3.346	6.726		35	h
SnSSe	3.729	6.074	0.036	28, 36	
NiSeTe	3.70	5.15		12	i
PdSeTe	3.90	4.98		12	i
PtSSe	3.59	5.06	0.00	13	
PtSTe				12, 13	
PtSeTe	3.890	5.110	-0.044	12, 13	

^a Lattice parameter for $x = 0.5$ in $\text{M}(\text{Ch}'_x\text{Ch}''_{1-x})_2$; a and c values in Å. ^b Δc is the deviation from linearity at $x = 0.5$; Δc values in Å. ^c Reference 25, only $x = 0.1$ prepared. ^d c parabolic, a linear for $0.82 < x < 1$; NbTe₂ structure for $0 < x < 0.31$. ^e Polyttype mixtures. ^f TaSeTe, only composition made (ref 32), has TaTe₂ structure. ^g At $x = 0.040$ phase change at $x \sim 0.075$. ^h At $x = 0.071$ phase change at $x \sim 0.071$. ⁱ NiSe₂ and PdSe₂ are not layered materials.

Table III. Mixed-Cation Systems

system	ref	system	ref
(Ti/V)S ₂	37-39	(V/Nb)Se ₂	33, 48, 49
(Ti/Cr)S ₂	37, 38	(Nb/Mo)Se ₂	10, 44
(Ti/V)Se ₂	40	(Ta/W)Se ₂	50, 51
(Ti/Ta)S ₂	41-43	(Fe/Ta)S ₂	52
(Ti/Nb)Se ₂	42-44	(Fe/V)Se ₂	53
(Ti/Ta)Se ₂	43	(Ta/W)S ₂	26
(Zr/Ta)S ₂	42	(Mo/W)Se ₂	10
(Zr/Sn)S ₂	45	(Hf/Nb)S ₂	4
(Hf/Ta)S ₂	46	(Hf/Mo)S ₂	4
(Zr/Sn)Se ₂	28	$\text{W}_{x/2}\text{Mo}_{x/2}\text{Ta}_{1-x}\text{Se}_2$	14
(V/Ta)S ₂	47	$\text{W}_{0.47}\text{Mo}_{0.47}\text{Ta}_{0.06}(\text{Se/Te})_2$	14

cupied sites between the layers are D_{3d} and C_{3h} , reminiscent of close packing. (For complete descriptions of these materials, and their relation to distorted-layer, marcasite, and pyrite-type dichalcogenides, see ref 10 and 11.) Although the crystallographic repeat distance may be many layers, we refer here to the hexagonal c parameter as the distance between adjacent metal layers. The a parameter is the length between metal atoms within a metal layer, d_1 defines the distance between chalcogen layers constituent to a sandwich, and d_g is the spacing of the gap between the chalcogen layers of adjacent sandwiches ($c = d_1 + d_g$).

From a survey of the lattice parameters for a large list of layered MCh₂ mixed systems, a clear trend emerges. The mixed-anion systems have a parabolic dependence of the c parameter on the mole fraction of chalcogen, and, with the exception of the platinum selenotellurium^{12,13} system, deviation from Végard's law is positive. The mixed-cation systems obey Végard's law. With the possible exception of mixed sulfur/tellurium systems, the a parameter varies linearly with com-

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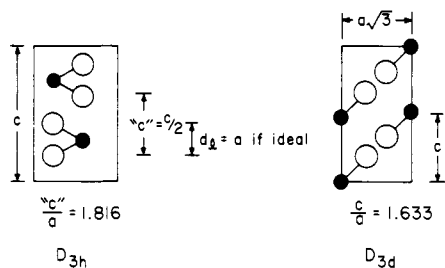


Figure 2. Derivation of ideal c/a ratios: ● = M, ○ = Ch in MCh_2 . Diagrams are (1120) projections.

position for all systems. (A possible additional exception is $Mo_{0.47}W_{0.47}Ta_{0.06}(Se_xTe_{1-x})_2$ where the c parameter is linear and the a is quadratic with composition.¹⁴) Tables II and III give the pertinent data and references for the mixed-anion and mixed-cation layered dichalcogenides.

In the formulation of a packing-mismatch model the central assumptions are stated as follows: The major part of the binding energy is derived from specific bonds, whose energy changes linearly with composition. The lattice relaxes to reduce the core repulsions of adjacent large atoms, which would otherwise overlap if a linear change in structure parameters were assumed for a linear change in binding energy.

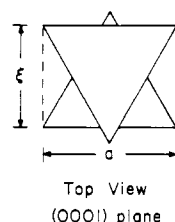


Figure 3. Relation of ξ , d_1 , d_g , c , and a for D_{3d} systems. The variables are a function of composition in mixed systems. ξ' , d_1' , d_g' , c' , and a' are the parameters for the $x = 1$ case in $M(Ch'_xCh''_{1-x})_2$, i.e., for the small-anion pure material. Double primes indicate the pure large-anion material, $x = 0$.

Since bond energy is less dependent on angle than length, bond lengths are assumed to change linearly while the lattice relaxes through a change in angle. In layered dichalcogenides, the a parameter is always more than the ionic diameter of the anion and much more than its covalent diameter. This means the anions are neither close packed nor bonded in the a direction. There is also slack between the layers bonded by weak van der Waals forces. Therefore, the major contribution to the bond energy is from the metal/chalcogen bond; we assume its length varies linearly with composition. We next consider these observations: The c/a ratio is generally less than that expected if a were the anion diameter and the structure were close-packed anions. This is true for both the D_{3h} and D_{3d} coordinated metals. For D_{3h} materials, the "ideal" c/a is derived from close-packed D_{3h} layers of thickness $d_1 = a$ (see Figure 2). For D_{3d} cases where the complete structure has been determined, the sandwich height is less than the gap height. Similarly in the D_{3h} materials the sandwich height is less than the a parameter, except for the 3% deviations in $2H-MoTe_2$ and $2H-TaSe_2$ (see pp 202–203 of ref 10). These trends suggest that, whereas these materials are not close packed in the a direction, they are close packed perpendicular to the layers. Forced by the linear composition dependence of the M–Ch bond, these close-packed anions relax perpendicularly to the layers when two (or more) of the larger anions would otherwise overlap. This results in the observed parabolic behavior of the c parameter in $Hf(Se_xTe_{1-x})_2$ and other mixed-anion systems.

Several qualitative predictions of this model can be compared to observations. As expected when series of the same mixed anions are compared, those with the largest change in the a parameter will show the smallest deviation from linearity of the c parameter; cf. the hafnium and titanium systems. In $Hf(Se_xTe_{1-x})_2$ the change in a parameter across the series is 0.2054 Å; at $x = 0.5$, the deviation from linearity in the c direction is 0.1237 Å. For $Ti(Se_xTe_{1-x})_2$, the numbers are 0.2350 Å and 0.0250 Å, respectively. A dramatic result of this behavior can be seen for $Pt(Se_xTe_{1-x})_2$. Here the change in the M–Ch bond length from $PtSe_2$ to $PtTe_2$ is large enough that the lattice relaxes by contracting; a negative deviation from linearity is observed.¹² This trend is not so clear for metallic materials, possibly due to a breakdown in the assumption that the M–Ch bond energy dominates the total

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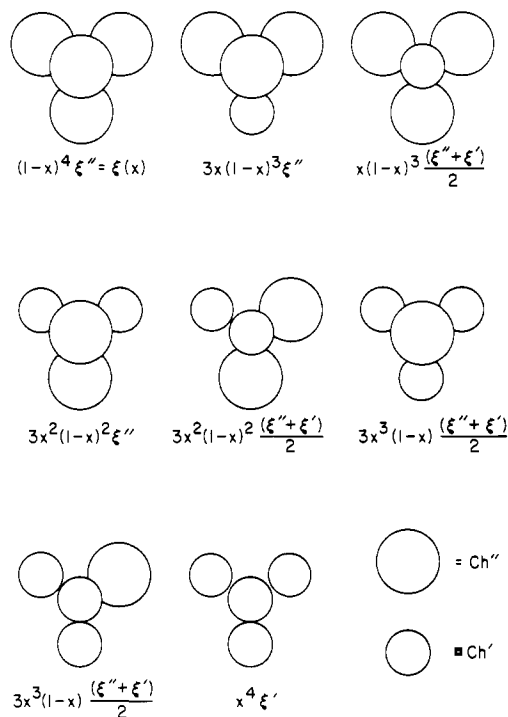


Figure 4. Possible mismatches for four interacting anions. The c axis is perpendicular to the paper, the tetrahedron viewed from above. Corresponding fraction and $\xi(x)$ are indicated below each repulsion cluster.

energy, i.e., metallic bonding energies are significant. Such bonding may in fact result in anions that are not close packed in the c direction. Indeed, the Végard's law deviation for the metallic systems is noticeably less than for the insulators. The largest deviations are seen in the more ionic insulators $\text{Hf}(\text{S}_x\text{Se}_{1-x})_2$ and $\text{Sn}(\text{S}_x\text{Se}_{1-x})_2$, where larger anion size implied by higher ionicity increases the chance of core repulsion. Finally, in $\text{Hf}(\text{S}_x\text{Te}_{1-x})_2$ and $\text{Ti}(\text{S}_x\text{Te}_{1-x})_2$, the size difference of the chalcogens is large enough that core repulsion can occur between telluriums in the a direction and a positive deviation in the a parameter is observed. However, these deviations are small when compared to those in the c direction.

More quantitative formulations of the packing mismatch are possible by explicitly writing the M–Ch linearity and c -direction relaxation in terms of the crystalline atomic spacing. The symbolic and geometrical relations for D_{3d} are given in Figure 3. (Our development is for D_{3d} layers but arguments for the D_{3h} case are analogous.) The first step is to choose the number of anion nearest neighbors that can result in core repulsions. We have already assumed that there is no close packing in the a direction of the anion layer. In addition, we assume that M–Ch linearity affects only repulsion in the sandwich, not between, due to the weak bonding between layers. This implies four nearest-neighbor anions, forming a distorted tetrahedron (C_{3h}), which can mismatch. There are eight possible tetrahedra in a mixed system $\text{M}(\text{Ch}'_x\text{Ch}''_{1-x})_2$ (see Figure 4), and the average ξ parameter (Ch'' – Ch'' distance in the layer; see Figure 3 for symbolic definitions) is given by eq 1a, where ξ' is ξ for MCh'_2 and ξ'' is ξ for MCh''_2 .

$$\xi_4(x) = x^4 \xi' + x^3(1-x) \xi^a + 3x^2(1-x) \xi^a + 3x^2(1-x)^2 \xi'' + 3x(1-x)^3 \xi'' + x(1-x)^3 \xi^a + (1-x)^4 \xi'' \quad (1a)$$

Substituting $(\xi' + \xi'')/2 = \xi^a$ and rewriting, we get eq 1b,

$$\xi_4(x) = \frac{1}{2}x(x^2 + 1)(\xi' - \xi'') + \xi'' \quad (1b)$$

where the subscript in $\xi_4(x)$ indicates four anions were assumed for possible repulsions in the calculation of the average ξ . The

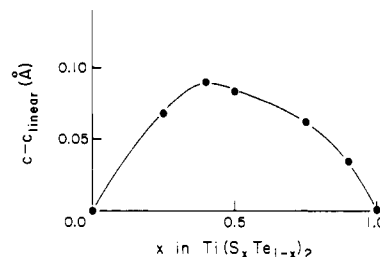


Figure 5. Deviation from linearity of the c parameter vs. composition for the series $\text{Ti}(\text{S}_x\text{Te}_{1-x})_2$ after ref 15.

general formulas for the average Ch' – Ch'' distance are given by eq 1c and 1d, and the deviations from a linear ξ are given

$$\xi_2(x) = \frac{1}{2}x(\xi' - \xi'') + \xi'' \quad (1c)$$

$$\xi_i(x) = \frac{1}{2}x(x^{i-2} + 1)(\xi' - \xi'') + \xi'' \quad i > 2 \quad (1d)$$

by eq 2a and 2b, where i is the number of anions in a repulsion cluster.

$$\Delta \xi_2(x) = 0 \quad (2a)$$

$$\Delta \xi_i(x) = \frac{1}{2}x(x^{i-2} - 1)(\xi' - \xi'') \quad (2b)$$

From Figure 3 we have eq 3a, and specifically for $i = 3$,

$$[c(x) - d_g(x)]^2 = \xi_i^2(x) - \frac{1}{3}a^2(x) \quad (3a)$$

4 we have eq 3b and 3c. It can be seen that for $i = 3$, $c(x)$

$$i = 3: [c(x) - d_g(x)]^2 = -\frac{1}{3}a^2(x) + [\frac{1}{2}x(x+1)(\xi' - \xi'') + \xi'']^2 \quad (3b)$$

$$i = 4: [c(x) - d_g(x)]^2 = -\frac{1}{3}a^2(x) + [\frac{1}{2}x(x^2 + 1)(\xi' - \xi'') + \xi'']^2 \quad (3c)$$

is of the order of x^2 , as is observed in the mixed systems, and for $i = 4$, which is the nearest neighbor scheme we assume, $c(x)$ is of the order x^3 . $d_g(x)$, ξ'' , and ξ' can be extracted by fitting the available data to eq 3c. However, due to the great variability of d_g , c , and a from material to material, such a procedure is dubious. However, a case by case comparison between formulation and behavior of specific systems can provide insight into the real nature of both the packing mismatch and the structure of these layered materials. Of immediate concern is the discrepancy between the observed x^2 and the predicted x^3 dependence for the c parameter. Since the deviation from linearity of the c parameter, $\Delta c(x)$, should behave roughly as the deviation in the $\xi_i(x)$, i.e., $\Delta \xi_i(x)$, for $i = 4$ the deviation of $c(x)$ will be skewed toward the compositions with a greater number of large anions:

$$\Delta c(x) \sim \frac{1}{2}x(x^2 - 1)(c' - c'') + c'' \quad (4)$$

Only for the most severe mismatch of anions, the system $\text{Ti}(\text{S}_x\text{Te}_{1-x})_2$, is such a dependence seen (see Figure 5). The observation of this skewness indicates the basic validity of our thesis. However, the failure to observe this for other systems implies that in general the assumptions are too rigid. In real materials the anion radii are not expected to behave like hard spheres of the model but rather yield slightly in repulsion interactions. Secondly, mismatches may relax in the a direction as well as the c direction. Since the anions are not close packed in the a direction, the average a parameter would still change linearly with composition. Finally, some of the mismatch in the layer may be washed out in the van der Waals gap between layers as the observed c parameter is the sum of both the layer and gap distances. Certainly more total structure determinations are desired.

Pyrites. The transition-metal dichalcogenides fall into two basic structural classes, layered and pyrite. Here, the mar-

casite structure is included in the pyrite class. The pyrite $\text{Co}(\text{S}_x\text{Se}_{1-x})_2$ exhibits a positive deviation from Végard's law,⁵⁴ consistent with the packing mismatch argument given for layered materials. However, the mixed-cation pyrites behave quite differently from their layered counterparts. The systems $\text{Fe}_{1-x}\text{Ni}_x\text{Te}_2$ and $\text{Fe}_{1-x}\text{Co}_x\text{Te}_2$ ⁵⁵ both show positive deviations from Végard's law. The dual series $\text{Fe}_{1-x}\text{Co}_x\text{S}_2$ and $\text{Co}_{1-x}\text{Ni}_x\text{S}_2$ show negative deviation if one plots the cubic a parameter vs. the number of electrons⁵⁶ from FeS_2 to NiS_2 . If the linear behavior of $\text{Fe}_{1-x}\text{Co}_x\text{S}_2$ is extrapolated to NiS_2 , this deviation can be viewed as a positive deviation for the nickel compound, and it is further indicated by the return to the $\text{Fe}_{1-x}\text{Co}_x\text{S}_2$ volume increase when additional atoms are added in the $\text{Ni}_{1-x}\text{Cu}_x\text{S}_2$ series. We feel the unusual behavior seen in the mixed-cation pyrites when compared to that of layered materials is a result of both the higher atomic density and the chalcogen-chalcogen bond present in the pyrites. This implies greater dependence of binding energy on structure and vice versa. When the atomic density of a pyrite is decreased, behavior closer to that of the layered materials is expected. This is apparently seen in the $\text{Cu}(\text{S}_x\text{Se}_{1-x})_2$ and $\text{Cu}(\text{Se}_x\text{Te}_{1-x})_2$ materials where the low-density copper pyrites exhibit negative deviation from Végard's law⁵⁷ similar to that seen in the

platinum systems. Such speculation would be answered by study of several mixed-structure systems, for example, the low-pressure phases of $\text{Fe}_{1-x}\text{Ni}_x\text{Te}_2$.

Some final comments and cautions on mixed dichalcogenides are in order. The synthetic details affect the homogeneities and stoichiometry of the product. Transport and mineralization reactions can improve stoichiometry but adversely affect both purity and homogeneity. Crystal quality can also be a function of composition. $\text{Hf}(\text{Se}_x\text{Te}_{1-x})_2$ exhibits good quality crystals for end members but poor crystal formation for intermediate compositions. The opposite is true for $\text{Mo}(\text{S}_x\text{Se}_{1-x})_2$.⁵⁸ Finally, one must remember that since most preparations are quenched from high temperature, the products reflect the thermodynamics at the growth temperature. This most likely explains the surprising lack of superstructure observed in these materials.

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Theoretical Study of the Structure and Stability of Oligomers of LiH

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The structure and stability of oligomers of lithium hydrides, $(\text{LiH})_n$ ($n \leq 8$), have been investigated by ab initio computations. Geometries are optimized by the energy gradient method. The calculation confirms as expected the strong tendency of lithium hydride to oligomerize. The equilibrium structure for the oligomers with the odd number of n is found to be planar cyclic with D_{nh} molecular geometry. On the other hand, the three-dimensional structures become more stable than the planar ones for oligomers with the even number of n , which point to the crystal structure. The features of geometrical parameters are also discussed in connection with the ionic character of the Li-H bond.

Introduction

The crystalline lithium hydride is a cubic system with a bond length of 2.045 Å, and it is known as a typical ionic crystal.^{1c} However, relatively few experimental and theoretical investigations of oligomers of LiH have been published until now. Experimentally only the dimer is identified by mass spectrometry and its atomization energy determined.² Theoretical studies³⁻⁵ have reported on the oligomers $(\text{LiH})_n$ ($n \leq 4$), and they predict planar cyclic structures with D_{nh} molecular symmetry although for the tetramer a three-dimensional T_d structure shows a comparable stability to the D_{4h} structure. More recently we have studied⁶ small lithium hydrides, Li_nH_m

($m \leq n \leq 4$), theoretically by referring to mass spectroscopic results of Li clusters⁷ and found that the lithium hydrides are stabilized by hydrogenation and that the oligomers of lithium hydrides, $(\text{LiH})_m$, are the most stable compounds in the series of Li_nH_m . We have also investigated the structure and the stability of the hexamer of LiH optimized by the energy gradient method.⁸ For the energy minimum configurations, we found the structural principle that the anion-anion distances are greater than those of cations, which causes the highly distorted three-dimensional structures.

In the present paper, we will report theoretical ab initio computations for the oligomers of lithium hydride, $(\text{LiH})_n$ ($n \leq 8$). We want to make clear the following problems: First, what are the equilibrium structures of the oligomers of the ionic molecules? Second, how large is the stabilization energy

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