Table I. Conductance of Chelated Aminedihydroaluminum(1+) Salts at 25°

	Λ, cm^2 equiv^{-1} ohm^{-1}	$10^2C^{1/2}$, $M^{1/2}$	Λ, cm^2 equiv^{-1} ohm^{-1}	$10^2C^{1/2}$, $M^{1/2}$
$(TMED)AlH_2^+I^-$ in HMPT	20.1	3.58	14.8	8.25
	18.2	4.98	16.1	8.44
	17.1	5.98	16.0	9.01
	16.2	6.25	16.2	10.4
	17.0	7.55		
$(TMED)AlH_2^+Br^-$ in HMPT	18.6	4.3	17.0	9.3
	15.5	4.6	17.0	9.6
	18.2	5.5	14.7	12.7
	18.2	5.9	15.3	13.2
	16.1	6.6		
$(sparteine)AlH_2^+I^-$ in MeCN	125.2	3.66	119.1	13.5
	130.6	6.01	109.2	16.7
	130.9	7.21		

$(L\text{-}L)AlH_2^+$ species. This is further supported by conductance measurements (Table I), wherein values of Λ are in the range reported for other 1:1 electrolytes in hexamethylphosphoric triamide[25] and acetonitrile,[26] respectively.

The observation of absorption, attributed to ν_{Al-H}, in TMED·$AlHBr_2$ at 1735 cm^{-1} suggests this to be a molecular complex with bonding similar to that of TMED·AlH_3.[17,18,24] Its low solubility in both solvents employed for conductivity measurements precluded an examination of its electrical conductance in solution.

The TMED·AlH_2Br complex exhibited absorption ν_{Al-H} at 1820 cm^{-1}, which is a frequency intermediate between that found for the dibromo analog and those of the cationic four-coordinate aluminum(1+) ions. In hexamethylphosphoric triamide, however, its electrical conductance is similar to that of TMED·AlH_2I, and, thus, in solution it appears to exist as the bromide salt of $(TMED)AlH_2^+$.

Although $(CH_3)_3N\cdot AlHI_2$ was not synthesized, the mixed haloalane adduct $(CH_3)N\cdot AlHBrI$ was prepared and utilized as a substrate in reaction with TMED. The resultant white solid product exhibited strong absorptions at 1893 and 1942 cm^{-1} but was thought to be a mixture of species and its characterization was not completed. Such absorption is in the region expected for cationic aluminum in four-coordination. In a purely speculative sense, the higher frequency band may suggest a divalent cation of the type $TMED[(CH_3)_3N]AlH^{2+}$. A selectivity of different halide ions to serve as leaving groups in nucleophilic displacement reactions has been reported for the formation of analogous chelated boron(*n*+) ions from the reaction of diamines with trimethylamine–haloboranes with iodide being more susceptible to displacement than bromide.[27] Similar selectivity may prevail in displacement from corresponding alane adducts.

As yet we have not explored the effect of the size of the bidentate amine on the rates of hydride oxidation or selectivity of these aluminum ions as reducing agents. As expected from the known relative reactivities of many hydrides of aluminum and boron, however, the aluminum salts hydrolyze with oxidation of hydridic hydrogen more readily than analogous boron(1+) salts such as $(TMED)BH_2^+I^-$. They are hygroscopic and evolve hydrogen rapidly on exposure to hydroxylic solvents.

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Registry No. $(TMED)AlH_2^+I^-$, 52628-93-0; $(TMED)AlH_2^+Br^-$, 52628-94-1; $(sparteine)AlH_2^+I^-$, 52628-84-9; $(CH_3)_3N\cdot AlH_2I$, 52628-90-7; $(CH_3)_3N\cdot AlH_2Br$, 52628-91-8; $(CH_3)_3N\cdot AlHBr_2$, 52628-92-9; TMED·$AlHBr_2$, 52628-85-0; $(CH_3)_3N\cdot AlHBrI$, 52628-89-4.

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Vapor Pressure of Samarium Diiodide and Mass Spectra of Vapors over Samarium Diiodide and Thulium Triiodide

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Mass spectrometric measurements show that $SmI_2(l)$ and $TmI_3(c)$ vaporize congruently in the Knudsen cell range as the monomolecular species. The second-law enthalpy of sublimation for $SmI_2(l)$ is $\Delta H_S{}^\circ{}_{298} = 69.5 \pm 2.0$ kcal/mol. The enthalpies of atomization for $SmI_2(g)$ and $TmI_3(g)$ are 171 ± 5 and 228 ± 5 kcal/mol, respectively. The enthalpies of formation of $SmI_2(c)$ and of $TmI_3(c)$ are $\Delta H_f{}^\circ{}_{298} \geqslant -141.0 \pm 5$ and -164.7 ± 5 kcal/mol, respectively.

Introduction

We earlier determined the vapor pressures over all of the stable lanthanide triiodides,[1,2] as well as that over SmI_3.[3] The mass spectra of the vapors over all of the triiodides, except that of TmI_3, also were determined.[4] These measurements showed that the lanthanide triiodides vaporize congruently as the monomeric LnI_3 in the Knudsen cell range, where Ln is the lanthanide. Recently, the vapor pressure and mass spectra of $EuI_2(l)$ were reported by Hariharan and Eick.[5] These workers showed that EuI_2 also vaporizes congruently as the monomeric diiodide. Comparison of the

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vapor pressure of EuI_2 with those of the stable triiodides shows that the latter materials are approximately 3 orders of magnitude more volatile. Also, the lanthanide iodides generally are more volatile than the bromides, chlorides, and fluorides, with the latter having much lower vapor pressures, and they are the only lanthanide halides which are stable against oxygen and moisture.

We here report on the vapor pressure of $SmI_2(l)$ and the mass spectra of the vapors over $SmI_2(l)$ and $TmI_3(c)$.

Experimental Section

Materials Preparation. Most of the SmI_2 was prepared by the direct reaction of iodine vapor with the metal contained in a tungsten crucible,[3] and some by the reaction of samarium with mercuric iodide.[6] Measurements of SmI_2 from both preparations gave identical results. The TmI_3 was prepared by the direct reaction of iodine vapor with the metal in a tungsten or tantalum crucible, with subsequent purification by sublimation. The starting lanthanide metals were of 99.9% purity. The iodine was a resublimed material of 99.99% purity. Analyses of SmI_2 showed 99.9% purity for the material prepared by direct reaction of the elements, while that prepared by the reaction of the metal with HgI_2 showed a purity of 99.7%. The TmI_3 was at least 99.9% pure.

All precautions were taken to prevent contact of the salts with the atmosphere during sample preparation and measurements.

Measurements. The vapor pressure of SmI_2 was measured, as described previously,[1] by effusion of the vapor from a tantalum Knudsen cell with orifices of 0.51- and 1.02-mm diameter. The effusion rate was measured on a Cahn microbalance, Model RH. The temperatures were controlled to within ±2°. Since molten SmI_2 has a tendency to creep up the wall of the Knudsen cell, less than 200 mg of material was used for each run. In order to ensure equilibrium conditions, tungsten chips were placed in the cell to increase the surface area of the molten salt.

The mass spectra were measured on a Bendix time-of-flight mass spectrometer, Model 12-101, with a Knudsen cell attachment supplied by Bendix. A tantalum cell with an orifice of 0.030 in. was used for these measurements. Details of the mass spectrometric measurements have been described previously.[4] The mass spectra were determined at 28 V, and the ionization efficiency curves of nitrogen and oxygen determined as internal standards for the determination of appearance potentials. The latter was determined by linear extrapolation with measurements at 0.5-V intervals.

Results and Discussions

Vapor Pressure of SmI_2. The vapor pressures of SmI_2 were calculated from the effusion rates of the monomeric species according to $SmI_2(l) \rightarrow SmI_2(g)$. The latter process was ascertained mass spectrometrically. The vapor pressures are summarized by the usual equation obtained by a least-squares fit

$$\log p_{\mathrm{atm}} = \frac{-13{,}367 \pm 275}{T} + 6.92 \pm 0.26 \qquad (1)$$

over a temperature range of 1008–1155°K. Figure 1 shows the plot of the data. There was no dependence of the vapor pressure on orifice dimensions. It may be interesting to note that the vapor pressure of SmI_2 is approximately twice as high as that of EuI_2.

The enthalpy of vaporization at the median temperature, calculated from eq 1, is $\Delta H_{1082} = 61.17 \pm 1.26$ kcal/mol. The mass spectrometrically determined value, $\Delta H_{1061} = 64 \pm 3$ kcal/mol, is in fair agreement with the above value. The enthalpy of vaporization was subsequently extrapolated to 298°K to obtain the heat of sublimation. The enthalpy functions used for this extrapolation were taken from Brewer, *et al.*,[7] for $SmI_2(c)$ and $SmI_2(l)$ and from Table I for $SmI_2(g)$.

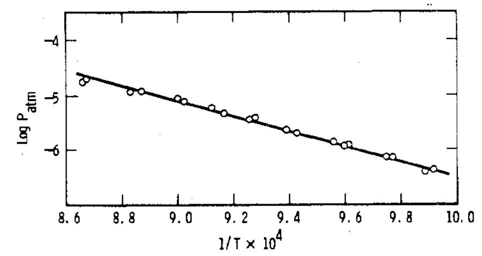

Figure 1. Logarithm of vapor pressures of $SmI_2(l)$ as a function of $1/T$.

Table I. Third-Law Thermodynamic Functions for $SmI_2(g)$

T, °K	C_p, cal/deg mol	$S°_T$, cal/deg mol	$H_T - H_{298}$, kcal/mol	$-(F - H_{298})/T$, cal/deg mol
298	15.87	84.44	0.0	84.44
800	16.29	100.35	8.11	90.21
1000	16.23	103.98	11.36	92.62
1200	16.07	106.93	14.60	94.76
1400	15.85	109.39	17.79	96.68

The data in Table I were obtained by third-law calculations for the gaseous diiodide by using the molecular constants of $LaI_2(g)$ reported by Krasnov and Timoshinin.[8] These constants are 190.5, 61.48, and 221.5 cm^{-1} for the vibrational frequencies, $r_e = 2.94$ Å, and a bond angle of 110°. A symmetry number of 2 was used in the calculation. For the electronic contribution, the method of Brewer, *et al.*,[9] was used by utilizing some 150 energy levels reported by Ofelt[10] and by Dupont.[11] The energy levels were arbitrarily truncated at the dissociation energy of $SmI_2(g)$, 7.4 eV. The estimated uncertainty in the free energy function is ±1.5 cal/deg mol.

For the second-law extrapolation, we used the $H_T - H_{298}$ values from Table I since heat capacity data for $SmI_2(g)$ are not available. Also, the extrapolation using the data from Table I should be as accurate as that obtained by using the heat capacity of a substitutional gaseous halide, as is the usual procedure. The second-law $\Delta H_S°_{298}$ thus obtained is 69.5 ± 2.0 kcal/mol. This value is in excellent agreement with 69.0 kcal/mol obtained by extrapolation using $\Delta C_p = -10$ cal/deg mol, as suggested by Brewer.[12] A third-law extrapolation also was made by using the free energy functions for $SmI_2(g)$ from Table I and for $SmI_2(c)$ and $SmI_2(l)$ by Brewer[7] and the measured vapor pressures. The $\Delta H_S°_{298}$ thus obtained is 71.5 ± 2 kcal/mol, with no temperature dependence of the extrapolated enthalpy of sublimation. The agreement between the second- and third-law extrapolations is satisfactory. Feber's[13] estimate of 70 kcal/mol is in excellent agreement with our value. In comparison, the second-law $\Delta H_S°_{298}$ for EuI_2 is 75.4 ± 1.1 kcal/mol.[5]

The free energy of vaporization at 1082°K, obtained from eq 1, is $\Delta G_{1082} = 26.9 \pm 1.3$ kcal/mol, and ΔS_{1082} is 31.7 ± 1.2 cal/deg mol.

The entropy of $SmI_2(c)$, $S°_{298} = 44.8$ cal/deg mol, was esti-

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mated by Latimer's method,[14] with corrections for magnetic contributions from Westrum.[15] The second-law entropy of sublimation of $\Delta S^\circ_{298} = 43 \pm 4$ cal/deg mol was obtained by using the $S_T - S_{298}$ data for SmI_2(c) and SmI_2(l) from Brewer[7] and for SmI_2(g) from Table I. Hariharan and Eick[5] reported an entropy of sublimation for EuI_2 of $\Delta S^\circ_{298} = 48$ cal/deg mol. Our entropy of sublimation for SmI_2 has a greater degree of uncertainty than that for EuI_2 because of the greater uncertainty in the entropy function of SmI_2(c) and SmI_2(l) used for the extrapolation. The entropy of SmI_2(g), $S^\circ_{298} = 88 \pm 4$ cal/deg mol, also bears this uncertainty. The agreement between the second- and third-law entropies appears satisfactory within the limits of uncertainty.

From the enthalpy and entropy of sublimation, the free energy of sublimation is $\Delta G_s{}^\circ_{298} = 56.7 \pm 2$ kcal/mol. The enthalpy of formation of SmI_2(c), determined from our mass spectrometric results and the enthalpy of sublimation (see below), is $\Delta H_f{}^\circ_{298} \geqslant -141 \pm 5$ kcal/mol. Combination of the latter value with the entropies for Sm(c),[16] I_2(c),[16] and SmI_2(c) yields a free energy of formation for the solid diiodide, $\Delta G_f{}^\circ_{298} \geqslant -140 \pm 5$ kcal/mol. The entropy of formation of SmI_2(c) is $\Delta S_f{}^\circ_{298} = 0.6$ cal/deg mol. Table II summarizes the thermodynamic properties of SmI_2.

The boiling point of SmI_2 was obtained by extrapolating eq 1 to 1 atm. The estimated boiling point is $T_B = 1932 \pm 33$°K. Brewer, *et al.*,[7] have tabulated the enthalpy of SmI_2(l) up to 1500°K. The extrapolation of the enthalpy above the latter temperature was made by using the $H_{1932} - H_{1500}$ value for PbI_2(l) given in the JANAF tables.[17] The experimental enthalpy of vaporization, ΔH_{1082}, was then combined with the estimated $H_{1932} - H_{1082}$ for SmI_2(l) and that for SmI_2(g) to obtain 50.8 ± 2.0 kcal/mol for the enthalpy of vaporization at the boiling point. Brewer[12] previously had estimated an enthalpy of vaporization of 40 kcal/mol and a boiling point of 1850°K. Both values are too low for SmI_2(l). Our enthalpy of vaporization is in agreement with 53.5 kcal/mol reported for EuI_2.[5] The entropy of vaporization, computed from our enthalpy of vaporization and boiling point, is $\Delta S_v{}^\circ = 26.3$ cal/deg mol. The value is nearly identical with 26.1 cal/deg mol reported for EuI_2.

Mass Spectra of SmI_2. The mass spectra of the vapor over SmI_2 were measured over the temperature range of 1051-1143°K. The relative intensity ratios of the ions were $I_{SmI_2{}^+}:I_{SmI^+}:I_{Sm^+} \approx 19:100:58$. The usual log *IT vs.* 1/*T* plot produced parallel lines for all of these ions, with a $\Delta H_{v\,1061} = 64 \pm 3$ kcal/mol. No ions arising from SmI_3 or polymeric species were detected. The vaporization, therefore, proceeds according to $SmI_2(l) \rightarrow SmI_2(g)$. The appearance potentials for $SmI_2{}^+$, SmI^+, and Sm^+ were 9.0, 9.8, and 13.1 eV, respectively, with an uncertainty of ±0.2 eV.[18] In comparison, the relative intensities for EuI_2[5] are $I_{EuI_2{}^+}:I_{EuI^+}:I_{Eu^+} \approx 34:100:81$, with appearance potentials of 8.8, 9.9, and 12.4 eV, respectively, for $EuI_2{}^+$, EuI^+, and Eu^+.

The enthalpy of atomization for SmI_2(g) was obtained from the relationship $D^\circ_0 \leqslant AP(Sm^+) - IP(Sm)$, where AP and IP are the appearance potential and ionization potential, respectively, for the parenthesized species. It is assumed that the products produced by electron impact do not have excess kinetic energy. Substitution of 13.1 eV for $AP(Sm^+)$ and 5.70 eV for IP(Sm)[19] yields $D^\circ_0 \leqslant 171 \pm 5$ kcal/mol (7.4 ± 0.2 eV). Combination of the latter value with the enthalpies of formation of Sm(g)[20] and I(g)[16] yields $\Delta H_f{}^\circ_{298}(SmI_2(g)) \geqslant -71.5 \pm 5$ kcal/mol. Since the sublimation enthalpy for SmI_2(c) is 69.5 kcal/mol, we obtain $\Delta H_{f\,298}(SmI_2(c)) \geqslant 141.0 \pm 5$ kcal/mol. Table III summarizes the mass spectrometrically obtained thermodynamic values.

Table II. Thermodynamic Properties of SmI_2[a]

	298°K				$T_B = 1932$°K	
	$\Delta H_f{}^\circ$	$\Delta G_f{}^\circ$	$\Delta H_s{}^\circ$	S°	ΔH_v	ΔS_v
SmI_2(c)	−141.0	−140	69.5	44.8		
SmI_2(g)	−71.5	−82		88		
SmI_2(l)					50.8	26.3

[a] Enthalpies and free energies in kcal/mol; entropies in cal/deg mol.

Table III. Enthalpies of Atomization and of Formation for Gaseous SmI_2 and TmI_3 (kcal/mol)

	D°_0	$\Delta H_f{}^\circ_{298}$
SmI_2	17 ± 5	−71.5 ± 5
TmI_3	228 ± 5	−92.5 ± 5

Table IV. Enthalpies of Formation of Positive Ions

	$\Delta H_f{}^\circ_{298}$ (±5), kcal/mol		$\Delta H_f{}^\circ_{298}$ (±5), kcal/mol
$SmI_2{}^+$	136	$TmI_3{}^+$	120
SmI^+	129	$TmI_2{}^+$	124
Sm^+	178	TmI^+	142
		Tm^+	202

Feber's[13] earlier estimates of $D^\circ_0 = 170$ kcal/mol and of $\Delta H_f{}^\circ_{298}(SmI_2(c)) = -140$ kcal/mol are in good agreement with the values reported here. Feber's values are based on the estimates of Brewer, *et al.*[7] (140 ± 7 kcal/mol), who derived their values from enthalpy of decomposition measurements reported by Jantsch and Skalla.[21]

Table IV summarizes the enthalpies of formation of the ions computed from the enthalpies of formation for SmI_2(g) and I(g).

Mass Spectra of TmI_3. The mass spectrum of the vapor over TmI_3 was determined only at 913°K. The spectrum was very similar in nature to those of the triiodides of the second rare earth subgroup.[4] The ion intensity ratios were $I_{TmI_3{}^+}:I_{TmI_2{}^+}:I_{TmI^+}:I_{Tm^+} = 50:100:37:51$. The ionization efficiency curves for the positive ions were very similar to those reported for the ions from DyI_3.[4] The appearance potentials for the ions $TmI_3{}^+$, $TmI_2{}^+$, TmI^+, and Tm^+ were 9.2, 10.5, 12.4, and 16.1 eV, respectively. These values are very similar to those of the positive ions obtained by electron impact of the other stable lanthanide triiodides. The above appearance potentials and the absence of any ions from polymeric species confirm the process $TmI_3(c) \rightarrow TmI_3(g)$.

The enthalpy of atomization of TmI_3(g), obtained from $AP(Tm^+) = 16.1$ eV and IP(Tm) = 6.22 eV,[19] is $D^\circ_0 \leqslant 228 \pm 5$ kcal/mol (9.9 ± 0.2 eV). Combination of this value with the enthalpies of formation of Tm(g)[20] and I(g)[16] results in the enthalpy of formation, $\Delta H_f{}^\circ_{298}(TmI_3(g)) \geqslant -92.5 \pm 5$

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kcal/mol. Since the enthalpy of sublimation of $TmI_3(c)$ is 72.2 ± 0.9 kcal/mol,[2] the enthalpy of formation of the solid triiodide is $\Delta H_f{}^\circ{}_{298}(TmI_3(c)) \geqslant -164.7 \pm 5$ kcal/mol. These thermodynamic values are summarized in Table III. Feber[13] reported low values of $\Delta H_f{}^\circ{}_{298}(TmI_3(c)) = -135.5$ kcal/mol and $D^\circ{}_0 = 201$ kcal/mol, based on the enthalpy of formation measured by Bommer and Hohmann.[22] The enthalpies of formation of the positive ions are summarized in Table IV.

Conclusions

The vapor pressures of the stable diiodides, *i.e.*, SmI_2 and EuI_2, are at least 2 orders of magnitude lower than those of the stable triiodides at temperatures below 1300°K. Although it is known that thulium, because of its electronic configuration, has properties which somewhat resemble those of samarium, there is no resemblance in the vaporization and mass spectroscopic properties of SmI_2 and TmI_3.

The thermodynamic properties estimated for SmI_2 and TmI_3 are consistent with values derived by other methods. The uncertainty in the second-law extrapolation of the entropy of sublimation for SmI_2 should be improved when heat capacity data become available for this compound.

Registry No. SmI_2, 32248-43-4; TmI_3, 13813-43-9.

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Constitution of Aluminum Base Rare Earth Alloys RT_2-RAl_2 (R = Pr, Gd, Er; T = Mn, Fe, Co, Ni, Cu)[1]

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The constitution of pseudobinary systems of the form RT_2-RAl_2 (R = Pr, Gd, Er; T = Mn, Fe, Co, Ni, Cu) is investigated by X-ray techniques. Earlier work had shown most of the binaries to crystallize with one of the Laves phase structures (C15). The ternaries RTAl are known to crystallize predominantly with the Fe_2P type or with another Laves phase variation (C14). The present work defines the composition limits and presents space filling in a systematic fashion. It is found that the extent of homogeneous regions of Laves phase compounds decreases from systems containing Mn to ones with Cu. Moreover, homogeneous regions are shifted toward binaries on the basis of Al with the heavier rare earths. Phase stability in these systems is discussed in terms of electronic and size effects. Beyond the systematic boundaries of this study some additional information is presented for systems RFe_2-RAl_2 and RCo_2-RAl_2 corroborating in a more general way the findings of shifts in phase boundaries to higher Al concentrations with heavier rare earths. Ag substitution in $PrAl_2$ was found to take place to a considerably larger extent than Cu substitution indicating an influence of size on phase stability. Anomalous behavior is observed in systems containing Pr and Mn. Appreciable deviations from Vegard's law indicate changes in valence. Pr appears to change from a predominantly 3+ ionic state in binaries to a 4+ state in pseudobinaries on the basis of Co and Ni. Mn appears to be 4+ in binaries and changes to 3+ in the pseudobinary region. Smaller deviations from Vegard's law in systems containing Fe and Co indicate ordering on crystallographic sites which has been corroborated by an independent X-ray study.

Introduction

The inorganic chemistry of Al-substituted compounds between rare earths and transition metals is of interest particularly on account of the many-faceted structural and magnetic behavior in the pseudobinary region of composition. Several stacking variations of binary structures as well as "missing" binary phases are often stabilized in the ternary region. Due to the broad homogeneous regions such alloys, moreover, are ideal study objects for the mechanism of magnetic exchange in spatially and electronically changing environments.[2] Furthermore, pseudobinary regions harbor several magnetic peculiarities. Of these the most outstanding concern a remaining, partial magnetic disorder below the magnetic ordering temperature and large anisotropy fields. Both effects combine to be responsible for unusually energetic domain walls at cryogenic temperatures.[3,4]

With this study we explore systematics of phase stability in pseudobinary sections of composition RT_2-RAl_2 with T = Mn, Fe, Co, Ni or Cu and with R = Pr, Gd, or Er. Al often behaves similarly to a transition metal in intermetallic compounds. Indeed most rare earth dialuminides as well as many RT_2 compounds crystallize with the cubic Laves phase ($MgCu_2$ or C15) structure.[5] Both binaries usually exhibit a considerable mutual solubility or, as in the case of some materials containing Mn, even complete miscibility. As a rule, however, a ternary phase, RTAl, intervenes, which with T = Fe and Co usually is of the $MgZn_2$ (C14) type[6,7] while with T = Ni and Cu the Fe_2P (C22) structure[8] is stable.

Both spatial and electronic factors are anticipated to contribute to stability and extent of homogeneous regions in these inorganic materials. Moreover, on Al substitution for T, electronic rearrangements are anticipated both on rare earths—particularly with representatives of the light rare earths (Pr)—and on transition metals. These electronic reconfigurations, or partial valence changes, if indeed present, are expected to manifest themselves in abnormal tendencies in lattice dimensions and in magnetic behavior. Such ab-

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[1] This study was, in part, supported by a grant from the Office of Naval Research.

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