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.

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Contribution from the Department of Chemistry,
University of California, San Diego, La Jolla, California 92037

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

HANS OESTERREICHER

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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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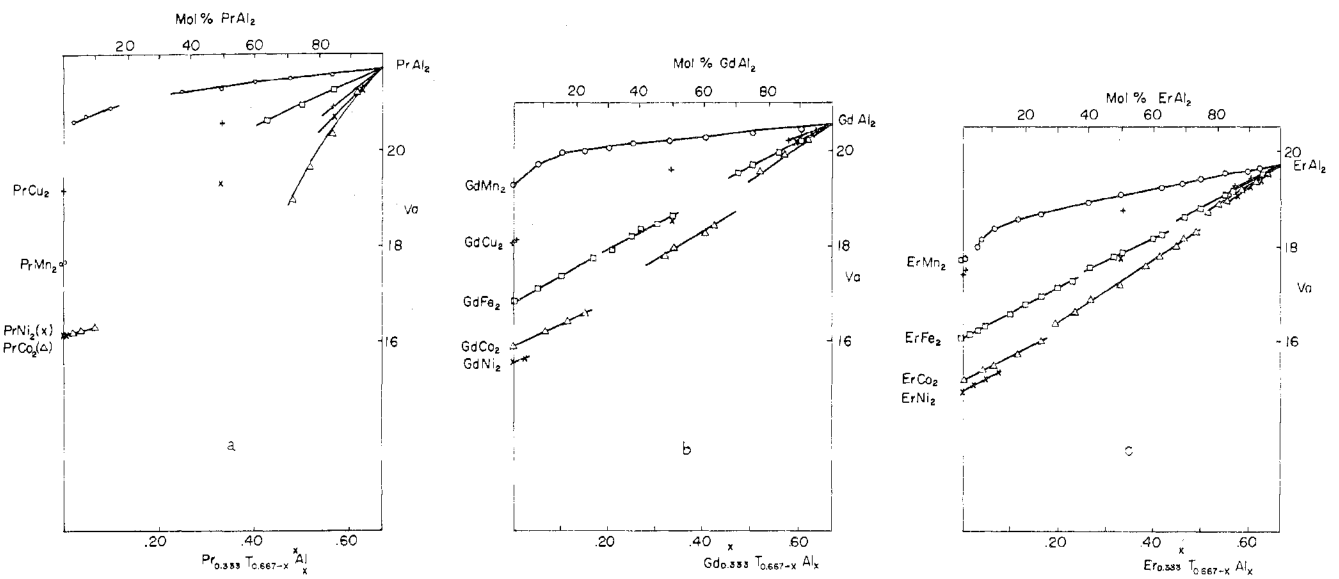

Figure 1. Average volume per atom (V_a) *vs.* concentration in pseudobinary systems of the form RT_2-RAl_2.

normalities have been recently reviewed by Wohlleben and Coles.[9]

The present study seeks clarification of the electronic state of the various components *via* space filling and phase stability arguments. It also should serve as a predictive scheme for phase stability and electronic character in related ternaries.

Experimental Section

The alloys were prepared in much the same way as previously described[2] by induction melting under Ar in MgO crucibles. In some cases the materials were subsequently annealed resting on MgO in evacuated silica ampoules. The rare earths were obtained from Michigan Chemical Corp. of Chicago and were 99.9% pure with respect to other rare earths or better than 99.5% total. Mn, Fe, Co, Ni, Cu, Ag, and Al had purities better than 99.999% and were obtained from American Scientific Chemical of Portland. Debye-Scherrer diagrams calibrated by means of NaCl were obtained with cameras using V-filtered Cr radiation. Phase changes were located by the appearance of lines characteristic of a new phase. Phase boundaries were obtained by breaks in the curves of volume per atom *vs.* composition.

Results

Crystallographic data are displayed in Figure 1 in terms of the average volume per atom (V_a) within the respective crystal structures plotted *vs.* the composition for systems containing Pr, Gd, and Er, respectively. Homogeneous regions of the various phases are shown systematically in Figure 2.

Several of the systems have been described earlier. Crystallographic data of $PrMn_2$-$PrAl_2$, $ErFe_2$-$ErAl_2$, and $ErCo_2$-$ErAl_2$ have been translated into values of V_a for the present study. In other cases additional experiments were carried out. Nowhere are the findings of the present study substantially at variance with earlier work.

In the following, we wish to outline the behavior of systems based on the individual rare earths in question.

Systems PrT_2-$PrAl_2$. Pseudobinaries PrT_2-$PrAl_2$ are clearly an exception from the general behavior in the series of rare earth systems in question. Of the binary RT_2 compounds only $PrCo_2$ and $PrNi_2$ are of C15 structure.[5] $PrMn_2$ crystallizes with the Th_6Mn_{23} structure at 1000° and can be written $Pr_6(PrMn)_{23}$.[10] $PrFe_2$ does not form at normal conditions although a pressure synthesis has been successful in stabilizing the C15 structure.[11] $PrCu_2$ is of $CeCu_2$ type structure.[12] There is also little regularity in the values of V_a of the various phases RT_2. $PrCu_2$ has the highest values of V_a and the two Laves phases $PrNi_2$ and $PrCo_2$ have the lowest. Homogenous regions of the pseudobinary systems $PrMn_2$-$PrAl_2$,[13] $PrCo_2$-$PrAl_2$,[14] and $PrNi_2$-$PrAl_2$[15] had been described earlier. For the sake of systematic comparisons, findings on alloys which had been prepared by quenching from the melt are presented. An exception is $PrMn_2$ which is single phase only after subsequent heat treatment (1000 K).

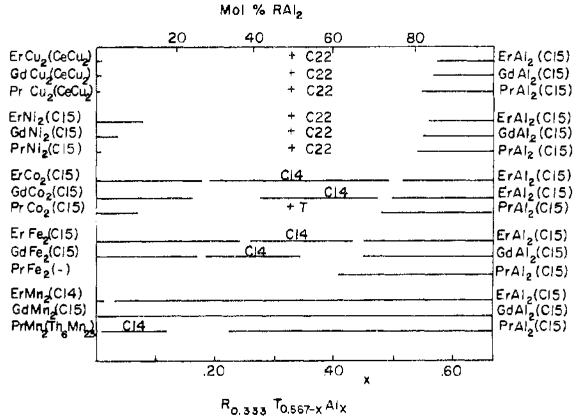

Figure 2. Homogeneous regions and crystal structures of systems RT_2-RAl_2.

Only $PrCo_2$ has an appreciable homogeneous region on Al substitution for Co. The increase in cell volume, however, is considerably smaller than the one expected from an extrapolation to the volume of $PrAl_2$. $PrMn_2$ of Th_6Mn_{23} structure has (at 1000 K) a very limited homogeneous region on Al substitution for Mn. The structure changes readily to the

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C14 type on further substitution (in both melted and annealed materials) connected with a dramatic increase in values of V_a. Other intermediary phases occur at compositions PrCuAl and PrNiAl (C22). PrCoAl is a single phase as shown by metallography and crystallizes with a yet unidentified structure.[6] The two C22 type phases exhibit values of V_a somewhat higher than the ones that would be arrived at from a linear extrapolation between the two respective binary phases. Transition metal substitution for Al in $PrAl_2$ takes place with slight positive curvature in values of V_a. The extents of homogeneous regions decline from Mn to Cu base systems but are appreciable in all cases.

Deviations from Vegard's law on substitution of T for Al change rapidly from Mn to Cu from strongly positive to negative ones. Only Ni-substituted alloys behave roughly ideally.

Several supplementary studies were carried out to ascertain the stability of intermediary compounds at lower temperatures. Annealing at 800° does not result in a change in structure of either PrCoAl and PrMnAl (C15) or PrNiAl and PrCuAl (C22). A similar heat treatment on the other hand does also not stabilize a homogeneous phase PrFeAl.

Systems GdT_2-$GdAl_2$. Compounds $GdMn_2$, $GdFe_2$, $GdCo_2$, and $GdNi_2$ are of C15 structure[5] and show a decrease in lattice dimension in the above order with a considerable step from $GdMn_2$ to $GdFe_2$. $GdCu_2$ has the $CeCu_2$ structure[12] with a value of V_a considerably larger than the ones of the analogous compounds with Fe, Co, and Ni.

All compounds with Gd and Er have been prepared by quenching from the melt. $GdMn_2$-$GdAl_2$ forms a continuous series of solid solutions with strong positive deviations from Vegard's law which are particularly pronounced toward $GdMn_2$. Similar observations were also made for analogous systems containing Tb, Dy, and Ho.[16]

Homogeneous regions decrease from Fe- to Cu-containing phases on Al substitution for T. In all these cases ternary phases intervene. While the C14 phases $GdFe_xAl_{2-x}$ show a considerable homogeneous region, the C22 type phases GdNiAl and GdCuAl show no homogeneous region within the limit of detection in our experiments. Values of V_a lie clearly above the ones expected from an extrapolation between the values of the binaries. $GdFe_2$-$GdAl_2$ behaves almost ideally with respect to space filling. There is perhaps a slightly positive deviation in V_a of Fe-substituted $GdAl_2$. $GdCo_2$-$GdAl_2$, on the other hand, shows relatively strong negative deviations from ideal behavior which are particularly pronounced toward the Al-rich phase boundaries of C15 $GdCo_2$ and C14 $GdCo_xAl_{2-x}$.

Systems ErT_2-$ErAl_2$. These systems are generally similar to the Gd analogs. An exception is $ErMn_2$-$ErAl_2$. $ErMn_2$ has the C14 structure but changes rapidly to C15 on Al substitution for Mn with familiar positive deviations from Vegard's law toward $ErMn_2$. No further phase change is observed. Ternary phases ErNiAl and ErCuAl are of C22 type and have no detectable homogeneous region. These phases again are relatively "open" structures compared with the Laves phase binaries. $ErFe_2$-$ErAl_2$, similar to its Gd analog, shows nearly ideal behavior while negative deviations exist in $ErCo_2$-$ErAl_2$ particularly toward the Al-rich phase boundary of C15 $ErCo_2$ and C14 $ErCo_xAl_{2-x}$.

Supplementary Studies. In order to compare more thoroughly trends in phase stability within systems containing other rare earths than dealt with so far in this study, we include some additional information, part of which had been published earlier. The phase boundaries of Table I were obtained with Fe- and Co-containing systems $R_{0.333}T_{0.667-x}$-Al_x which had been prepared by quenching from the melt. The findings on Fe-containing systems agree well with the ones of a study by Dwight, *et al.*[17]

Table I

R	x		
	C15	C14	C15
	$R_{0.333}Fe_{0.667-x}Al_x$		
Pr			0.400
Nd			0.350
Sm	0.160	0.190–0.332	0.360
Gd	0.175	0.190–0.344	0.400
Tb	0.190	0.215–0.346	0.403
Dy	0.215	0.235–0.375	0.415
Ho	0.230	0.248–0.395	0.431
Er	0.242	0.255–0.425	0.445
	$R_{0.333}Co_{0.667-x}Al_x$		
Pr	0.053		0.528
Sm	0.160	0.215–0.456	0.490
Gd	0.160	0.200–0.480	0.495
Tb	0.165	0.189–0.480	0.500
Dy	0.170	0.189–0.485	0.505
Ho	0.175	0.190–0.490	0.510
Er	0.179	0.194–0.500	0.520

In view of recent findings (Kimball, *et al.*[18]) of phase transitions from the hexagonal densely packed C14 structure to the relatively open C22 structure at lower temperatures (in the region of 800°) we have annealed some C14 materials at 600°. Both TbFeAl and DyFeAl (C14) do not undergo a change in crystal structure on this low-temperature heat treatment.

For the sake of discussion of electronic and spatial effects responsible for the various homogeneous regions, it was, finally, of interest to include one system containing Ag which is isoelectronic with but larger than Cu. Ag substitution for Al takes place up to about a composition $Pr_{0.333}Ag_{0.22}Al_{0.447}$ in materials which had been obtained by quenching from the melt. Ag and Al are nearly comparable in atomic radius and so it is not surprising that no appreciable change in lattice parameter could be observed on Ag substitution for Al. The phase boundaries in this instance, therefore, are established not by extrapolation to a constant lattice parameter but by the appearance of a new phase. The accuracy is about $x = \pm 0.02$ in this case. There is no ternary phase at a composition PrAgAl.

Systematic Comparison of Phase Boundaries. Phase boundaries of pseudobinary sections in RT_2-RAl_2 with R = Pr, Gd, or Er and with T = Mn, Fe, Co, Ni, or Cu are presented in a systematic fashion in Figure 2. It is clearly seen that homogeneous regions of both C15 types RT_2 and RAl_2 increase from systems with T = Cu to the ones with T = Fe. An exception is $PrFe_2$ which does not form under normal conditions.

Judging from phase boundaries of the three rare earths in question the heavier rare earths appear to have the largest homogeneous regions on Al substitution in RT_2 compounds while it is the compounds RAl_2 with the lighter rare earths which take up more transition metal. The largest homogeneous regions are observed on Mn substitution in RAl_2 compounds completing the trend of larger homogeneous

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regions with the lighter transition metals in question. In this case, however, it is $GdAl_2$ which takes up the most transition metal while $PrAl_2$ has the smallest homogeneous region. On the Mn-rich side the situation is more complex in that the C14 phase $PrMn_xAl_{2-x}$ appears at concentrations richer in Al than $ErMn_xAl_{2-x}$ while $GdMn_2$-$GdAl_2$ forms a complete series of solid solutions of the C15 type.

Discussion

It appears from the preceding data that both size and electronic effects are responsible for the varying stabilities of rare earth compounds with Al and transition metals. Size effects manifest themselves, particularly, in the dependence of homogeneous regions on the rare earths in question since in a straightforward model rare earths can be assumed to be tripositive. Homogeneous regions of compounds RT_2 appear to be the larger the smaller the rare earth in question, while the opposite is true for the aluminides.

Electronic effects are apparent when one compares the dependence of extent of homogeneous regions on the transition metal. The stability of Laves phases increases systematically from alloys containing Cu to the ones with Mn although the atomic radii of these transition metals change very little and show a small minimum with Ni.

The electronic and spatial effects are difficult to separate. To begin with, the assumption of a constant valency of the rare earth is somewhat questionable. This is particularly so with the lighter rare earth as we will outline further below for the case of Pr. It ought even to be taken with reservations with such "simple" rare earths as Gd and Er. Matthias, *et al.*,[19] for instance, have suggested that the low melting points of light lanthanides are due to the presence of some f character in the hybridized wave functions describing the band structure for the band electrons. This implies a varying character of the overall band structure within various rare earths. This model has been elaborated on by Gschneidner,[20] who postulated that there are two kinds of 4f electrons—atomic 4f electrons and 4f band electrons. 4f band electrons occur because the lowest of the empty energy levels, which vary from 14 for La to 1 for Tm, lies very close to the Fermi level and thus is partially occupied by valence electrons. According to Gschneidner 4f band electrons vary from 0.7 for the light rare earth to about 0.1 for the heavy. The different character of electrons at the Fermi level may well have an influence on phase stability—in addition to size factors—and explain the progression from larger to smaller homogeneous regions with heavier or lighter rare earths.

Other, although equally controversial, evidence for size factors operating in the stabilization of broad homogeneous regions is found when the effects of Cu and Ag substitution in $PrAl_2$ are compared. While C15 $PrAl_2$ breaks down on Cu substitution for Al at a composition $Pr_{0.333}Cu_{0.127}Al_{0.540}$, the C15 structure is stable up to a composition $Pr_{0.333}Ag_{0.22}$-$Al_{0.447}$ on Ag substitution. The considerably larger homogeneous region on Ag substitution in $PrAl_2$ would naturally follow from the nearly comparable atomic radii of Ag and Al (1.44 and 1.43 Å, respectively) compared with the smaller one of Cu (1.28 Å). On the other hand, it is well known that the conduction electrons of the heavier atoms Ag and Au have considerably more d-electron character than the ones of Cu. This again could well result in different criteria for phase stability. It is indeed difficult to separate unambiguously the influences of spatial and electronic factors when both are changing within the periodic table in such a congenial way.

The fact that the Laves phases have comparable packing arrangements (Wallace[21]) but show few regularities concerning the size of components (Dwight[22]) is commonly taken as evidence for the predominance of electronic factors over the ones of size governing the stability for this family of compounds. Accordingly Elliott and Rostocker[23] have analyzed the occurrence of Laves phases in terms of a model of bands of stability in which the C15 and C14 type alternate when the electron concentration is systematically changed. If the electron concentration is near the border of a band of stability, more complex stacking variations often occur.

Since the electron concentration undoubtedly changes in the pseudobinary systems in question, the alternating occurrence of C15, C14, and C15 types particularly of Fe- and Co-containing systems is one further example for this regularity. In fact the phase boundaries of Co-containing rare earth systems have been previously explained in a quantitative fashion by Oesterreicher and Wallace[24] in terms of Fermi surface Brillouin zone interactions.

It was concluded that the C15 type RCo_2 becomes unstable at a characteristic electron concentration which corresponds to the filling by Fermi electrons of Brillouin zones formed by planes {220} and {111}. To arrive at that conclusion it was assumed that both Fe and Co absorb electrons into their d shell. Since Fe can absorb more electrons, the phase boundary occurs at a higher Al concentration. This model, however, does not explain the extent of homogeneous regions at higher Al concentrations.

The assumption of a negative rather than positive valence of Fe and Co (corresponding to an absorption of electrons into d bands of Fe and Co) was invariably corroborated by the declining magnetic moment of the transition metal on partial substitution by Al for T, a various pseudobinary systems.[2-4] If one takes the vanishing values of magnetic moment at Fe sites at face value, one has to conclude that Fe does not exist as positive ion, say Fe^{3+}, with its concomitant magnetic moment corresponding to a d^5 configuration. A tripositive Fe on the other hand would comfortably explain the crystal chemical similarity of Fe and Al demonstrated in the present study.

In any case the appearance of broad homogeneous regions within representatives of the Laves phases seems to depend on one component having an unfilled d shell. When the d shell is filled completely (Cu) or nearly so (Ni), the intermediate phase is of the relatively open C22 structure and the binaries on transition metal basis either have limited homogeneous regions or do not have the Laves phase structure altogether.

A comprehensive study on systems RFe_2-RAl_2 has recently appeared (Dwight, *et al.*[17]). As an unexpected feature it was found that the boundaries between the three areas of phase stability exhibited a pronounced curvature. For the heavy rare earths the boundary between regions of stability of $MgCu_2$ type and $MgZn_2$ type compounds is rather flat, which indicates a sensitivity to the atomic volume of the rare earth element. Indeed a retrograde curvature was found

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toward the highest and lowest V_a, particularly with Pr and Sc alloys. The present study corroborates these effects for both systems RCo_2-RAl_2 and RFe_2-RAl_2.

One of the most striking features of the present investigation concerns the aberrant behavior of volumes per atom in systems containing either the rare earth Pr or the transition metal Mn. Strong negative deviations from Vegard's law are observed, particularly in systems $PrNi_2$-$PrAl_2$ and $PrCo_2$-$PrAl_2$. In these systems it appears as though deviations from the ideal binary solution behavior are due to a gradual change of valence of Pr from 3+ to 4+. The opposite is observed on Fe and Mn substitution for Al in $PrAl_2$.

It may be of interest in this connection to discuss the relevance of these findings to the problem of hydride formation. Hydrogen has been recently found to be absorbed in $CaCu_5$ type materials (*e.g.*, $LaNi_5$) easily and reversibly at a few atmospheres of pressure (van Vucht, *et al.*[25]). In $CeNi_5$, however, hydrogen did not dissolve up to relatively high pressure, presumably due to the 4+ ionic nature of Ce in this material. Judging from the findings of the present study Fe substitution may counteract ionization into the 4+ state possibly on account of size factors. Moreover, electron transfer from Al to Fe should result in a relatively filled d-shell configuration ("pseudo Ni"). This configuration appears to facilitate hydrogen take-up. Suitably substituted alloys on the basis of Ce, Pr, Fe, Ni, and Al, therefore, may become of technological interest as hydrogen storage materials.

Alloys containing Mn uniformly show positive deviations from Vegard's law. Moreover, values of V_a drop considerably toward the Mn-rich phase boundary. Magnetic studies show that Mn is either in its 3+[14] or 4+[26] state in Laves phase intermetallics. The tendencies in V_a, therefore, would seem to indicate that toward binaries RMn_2, Mn changes from the 3+ to 4+ ionic state. The pronounced step in values of V_a from C14 $PrMn_xAl_{2-x}$ to $PrMn_2$ (Th_6Mn_{23} structure) would seem to indicate considerable electronic rearrangement on both Pr and Mn. $PrMn_2$ has been investigated magnetically[27] but the situation is too complex to allow for conclusions concerning the electronic nature of both constituents.

While transition metals Fe, Co, Ni, and Cu can be considered to contribute less to the delocalized electrons than Al, Mn is of either comparable or higher valence. The stability of C14 structures $PrMn_xAl_{2-x}$ and $ErMn_xAl_{2-x}$, therefore, appears to involve different electronic criteria than the one of Fe- and Co-containing compounds.

The discontinuities in V_a between C15 and C14 materials observed most pronouncedly with Co-containing pseudobinaries indicate an improved packing efficiency which in turn suggests an ordered arrangement between T and Al. In the C14 structure ordering is possible on 2a and 6h sites. In an independent X-ray study we have shown that at the Al-rich phase boundary ordering between Al and Co does indeed occur with Co occupying site 2a. This corresponds to a superstructure of $MgZn_2$ which can be written R_2TAl_3.[28]

When T = Fe, tendencies for ordering are less pronounced. Again the transition metal tends preferentially to occupy 2a sites but now only at the Al-poor phase boundary. At the Al-rich phase boundary no deviation from random occupancy between Fe and Al was observed. Similar conclusions were also drawn on evidence from Mossbauer spectroscopy.[17] Only with the rare earths does the T element prefer the 2a site. Several examples of a superstructure to $MgZn_2$ are known, for instance, U_2Fe_3Al,[17] Nb_2Co_3Ge,[29] or Mg_2Cu_3Si,[30] but in these cases the T element occupies the 6h site.

Registry No. $ErCu_2$, 12527-58-1; $GdCu_2$, 12527-59-2; $PrCu_2$, 12310-79-1; $ErNi_2$, 12192-18-6; $GdNi_2$, 12024-74-7; $PrNi_2$, 12201-94-4; $ErCo_2$, 12017-20-8; $GdCo_2$, 12017-22-0; $PrCo_2$, 12017-40-2; $ErFe_2$, 12020-15-4; $GdFe_2$, 12023-08-4; $PrFe_2$, 12305-97-4; $ErMn_2$, 12020-20-1; $GdMn_2$, 12024-68-9; $PrMn_2$, 12311-59-0; $ErAl_2$, 12004-20-5; $GdAl_2$, 12004-26-1; $PrAl_2$, 12043-24-2.

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Contribution from Rocketdyne, a Division of Rockwell International,
Canoga Park, California 91304

Halogen Nitrates

KARL O. CHRISTE,* CARL J. SCHACK, and R. D. WILSON

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The low-temperature infrared and Raman spectra of $I(NO_3)_3$ and the Raman spectra of liquid $ClONO_2$, $FONO_2$, FNO_2, and $ClNO_2$ have been recorded. Comparison of the vibrational spectra within the series NO_2, FNO_2, $ClNO_2$, $FONO_2$, and $ClONO_2$ allows unambiguous assignments for the halogen nitrate molecules. Raman polarization measurements show that in halogen nitrates the halogen atom is perpendicular to the ONO_2 plane contrary to previous assumptions and to the known planar structure of $HONO_2$ and CH_3ONO_2. The vibrational spectrum of $I(NO_3)_3$ is consistent with predominantly covalent nitrato ligands. However, the complexity of the spectrum suggests a polymeric structure with bridging nitrato groups. Experimental evidence was obtained for the formation of the new and thermally unstable compound $CF_3I(NO_3)_2$ in the CF_3I-$ClONO_2$ system. Attempts to convert this compound into CF_3ONO_2 were unsuccessful.

Introduction

Highly electronegative groups such as perchlorates, nitrates, fluorosulfates, or trifluoroacetates can be considered as pseudohalides. As such they either can form stable anions in the presence of suitable cations or can act as covalent ligands particularly when bonded to highly electronegative elements such as the halogens or oxygen. Whereas the vibrational spectra of the free anions are relatively well understood, those of the corresponding covalent ligands have only recently received more attention. Reliable spectra and assignments