50-8; Zn, 7440-66-6; Cd, 7440-43-9; Ag, 7440-22-4; Hg, 7439-97-6; tde, 111-48-8; tht, 110-01-0; des, 352-93-2.

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Infrared Matrix Isolation Studies of the $M^+SiF_5^-$ Ion Pair and Its Chlorine–Fluorine Analogues

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The matrix isolation technique has been applied to the study of the $M^+SiF_5^-$ ion pair, as a model for possible intermediates in organosilicon reactions. This ion pair, formed through the reaction of an alkali fluoride salt and SiF_4, showed six infrared bands, three in the Si–F stretching region and three in the deformation region. This spectrum is inconsistent with a strictly trigonal-bipyramidal D_{3h} geometry for the species, but a model in which the cation perturbs the anion axially yielding a C_{3v} species can account for the observed spectrum, although C_{2v} and C_{4v} structures are considered as well. The mixed chlorine/fluorine anions were synthesized also, by reaction of either MF or MCl with the appropriate precursor species. However, attempts to synthesize the $SiCl_5^-$ anion in this fashion were not successful.

Introduction

A large segment of synthetic organosilicon chemistry has been developed around the use of the fluoride anion, F^-, as a catalyst in these systems.[1,2] It has been proposed that the mechanism of this catalysis proceeds through a pentacoordinate silicon intermediate and then to products.[3] Recently, pentacoordinate silicon anions have been synthesized and stabilized, but very little is known about the nature, geometry, and stability of these anions. Ion cyclotron resonance[4,5] has been employed to give some heats of formation and the

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fluoride ion affinity of SiF_4, but further information is necessary concerning these possible reaction intermediates.

Ten years ago, the first synthesis of the pentacoordinate silicon anion SiF_5^- in crystals was carried out, and the spectra obtained were consistent with a trigonal-bipyramidal geometry.[6,7] This anion may be viewed as the simplest of the pentacoordinate silicon anions, and further study of this anion is warranted as a model for general pentacoordinate silicon anions as reaction intermediates.

The salt/molecule reaction technique has been coupled with the matrix isolation technique in recent years to allow for the synthesis of ion pairs isolated in inert matrices at low temperatures.[8-10] In this technique, an alkali halide salt molecule is vaporized from a high-temperature oven and codeposited with a Lewis acid, so that halide anion transfer from the salt molecule to the Lewis acid occurs, forming an isolated ion pair. To date, only triatomic anions have been synthesized and investigated in this manner, but the extension of this technique to larger anions should be straightforward. With the interest in pentacoordinate silicon anions and the availability of the salt/molecule reaction technique for low-temperature synthesis, a study was undertaken to investigate the $M^+SiF_5^-$ ion pair and its chlorine derivatives in argon matrices.

Experimental Section

All of the experiments described here were conducted by using a conventional matrix isolation apparatus, which has been described previously.[11] The salts employed in this study were KF (Fisher), CsF (Alfa), KCl (Allied, reagent), and CsCl (Fisher). The salts were loaded in a stainless steel Knudsen cell and outgassed under vacuum behind a closed door before the beginning of an experiment. Oven temperatures for the various salts were as follows: KF, 650 °C; CsF, 500 °C; KCl, 550 °C; CsCl, 500 °C. SiF_4 (Matheson) and $SiCl_4$ (Fisher) were distilled under vacuum, through two freeze/thaw cycles, prior to sample preparation. Argon was used as the matrix gas and was used without further purification.

The mixed chlorine–fluorine species $SiClF_3$, $SiCl_2F_2$, and $SiCl_3F$ were synthesized according to literature procedures,[12] through the fluorination of $SiCl_4$ by SbF_3 in the presence of $SbCl_5$. A mixture of gases was collected from this reaction and distilled on a vacuum line to partially separate the various products. Complete separation of the mixed chlorine–fluorine species was not achieved, and samples prepared in this manner for matrix experiments contained a mixture of parent species.

Matrix samples were deposited for 20–24 h before final spectra were recorded on a Beckman IR-12 infrared spectrophotometer. Both survey scans and high-resolution scans over the region of interest were recorded. In some experiments, the sample was then warmed to about 40 K to allow diffusion and then recooled to 15 K and further spectra were recorded.

Results

Before the reaction products of alkali halide salts with SiF_4 were recorded, two blank experiments were conducted, in which samples of $Ar/SiF_4 = 400$ and 150 were deposited and spectra recorded. In each case, a very intense band near 1025 cm^{-1} assignable to ν_3 was observed, with several low-energy satellites, due to silicon isotopes, as well as slight aggregation, especially at $M/R = 150$. In addition, a moderately intense band was observed at 385 cm^{-1}, corresponding to ν_4 of SiF_4. In several experiments, a weak band was also detected at 820 cm^{-1}, apparently due to slight impurity of OF_2.

CsF + SiF_4. CsF was codeposited with samples of Ar/SiF_4 in three different experiments, at M/R values of 150, 400, and 1000. Six bands were observed in each of these experiments, three in the upper, stretching, region between 800 and 950 cm^{-1} and three in the lower, bending, region, 400–500 cm^{-1}. The three upper bands, at 932, 855, and 812 cm^{-1}, were all relatively intense, and certainly more intense than the low-energy bands, which we located at 444, 457, and 480 cm^{-1}. More importantly, all six bands showed a constant intensity ratio to one another in all three experiments, over a large range in concentration. In the most concentrated experiment, at $M/R = 150$, two weak bands appeared as low-energy satellites on the 812-cm^{-1} band, at 805 and 799 cm^{-1} with relative intensities of these three bands 812:805:799 cm^{-1} of 8:1:1, indicative of silicon isotope splitting.

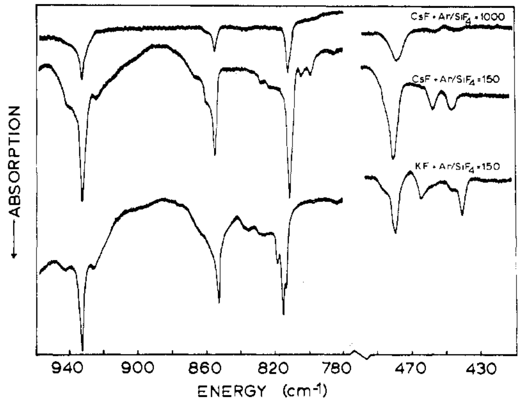

Figure 1. Infrared spectra of the reaction products of CsF and KF with samples of Ar/SiF_4, at different dilution ratios over the spectral regions of interest.

In the experiment using intermediate concentrations, $M/R = 400$, the sample was annealed after final spectra were recorded. When the matrix was heated to around 35 K to allow slight diffusion, all six bands grew, and in the same ratio. However, when the matrix was warmed further, to around 45 K to allow complete diffusion, all six bands decreased to almost zero, and an intense band grew in near 730 cm^{-1}. Comparison to literature spectra indicates that this band can be assigned to the well-known Cs_2SiF_6 species.[13] This band persisted even after the cold window had been warmed to room temperature and all volatile species were pumped off.

KF + SiF_4. KF was codeposited with Ar/SiF_4 in a single experiment, and again six distinct product bands were detected, shifted only slightly from the band positions in the analogous Cs experiment. These bands were located at 935, 854, and 816 cm^{-1} in the upper region, and at 480, 464, and 440 cm^{-1} in the lower region. These bands also showed similar relative intensities to the bands observed in the analogous Cs experiment. The spectra of the reaction products of CsF and KF with SiF_4 are shown in Figure 1.

CsCl + SiF_4. CsCl was codeposited with a sample of Ar/SiF_4 in one experiment, and several weak product bands were detected. However, the overall yield in this experiment was low, and only bands in the stretching regions were detected. The most intense band was located near 808 cm^{-1}, with splittings on the low energy side, as well as weak bands at 932, 902, 879, and 570 cm^{-1}.

$SiCl_4$. Before any reactions were carried out employing $SiCl_4$, a blank experiment of $Ar/SiCl_4 = 400$ was carried out and revealed intense bands at 620 and 642 cm^{-1} (split components of ν_3), as well as a medium-intensity band at 220 cm^{-1}, corresponding to ν_4.

CsF + $SiCl_4$. CsF was codeposited with $Ar/SiCl_4$ in two experiments, at $M/R = 400$ and 150. The results were quite similar in these two experiments, with slightly more overall intensity in the $M/R = 150$ experiment. Three product bands were observed in the spectrum, at 769, 558, and 499 cm^{-1}, and these three bands showed a constant intensity ratio in the two experiments performed.

CsF and CsCl + Mixed $SiCl_xF_y$ ($x + y = 4$). Ten experiments were conducted in which either CsF or CsCl was codeposited with a sample of mixed precursor. The mixed precursors $SiClF_3$, $SiCl_2F_2$, and $SiCl_3F$ could not effectively be separated from one another or from the perfluoro and perchloro compounds, so that a number of different species were

Table I. Band Positions and Assignments for Stretching Vibrations of the $Cs^+SiF_5^-$ Ion Pair and Its Mixed Chlorine/Fluorine Derivatives[a]

ν, cm^{-1}					
SiF_5^-	$SiClF_4^-$	$SiCl_2F_3^-$	$SiCl_3F_2^-$	$SiCl_4F^-$	assignment[b]
932	932	928	925		ax Si–F str
855	902, 879				eq Si–F str
812	802	787	779	769	br Si–F str
	570	567	563	558	eq Si–Cl str
				499	ax Si–Cl str

[a] Assignments based on C_{3v} model. [b] Key: ax = axial, eq = equatorial, br = bridging, str = stretch.

present in any given experiment. However, the relative amounts of F and Cl present could be adjusted, so that CsF, for example, could be deposited with a sample containing mainly SiF_4 and $SiClF_3$. A number of different cross products were studied, and the results can be summarized as follows: When CsF was codeposited with a sample containing mainly SiF_4 and $SiClF_3$, the predominant bands were located at 932, 855, and 812 cm^{-1}, as detected in earlier experiments involving CsF and SiF_4. In addition, a weak band was observed at 802 cm^{-1} in addition to a broad, weak band with apparent maxima at 787, 779, and 769 cm^{-1}.

When CsF was codeposited with a mixture of precursors with a higher Cl/F ratio, being predominantly $SiCl_4$ but also containing roughly equal amounts of $SiCl_3F$ and $SiCl_2F_2$ and lesser amounts of $SiClF_3$ and SiF_4, the same sequence of bands was observed, ranging from 812–801 cm^{-1} to the 787-, 779-, and 769-cm^{-1} band, which was observed earlier in the reaction of CsF with $SiCl_4$. This latter band was the most intense in this portion of the spectrum. Weak bands were also detected at 928 and 925 cm^{-1} in this experiment.

Codeposition of CsCl with mixed samples which contain $SiCl_4$ predominantly showed this same band sequence, with slightly shifted positions to 793 and 777 cm^{-1} from 787 and 779 cm^{-1} observed earlier, as well as two weak bands at 925 and 928 cm^{-1}. Similarly, codeposition of CsCl with a sample containing SiF_4 predominantly and slight amounts of $SiClF_3$ showed a band at 808 cm^{-1}, as observed earlier in the reaction of CsCl with SiF_4, as well as a broad hint of a band or bands from 770 to 790 cm^{-1}, but not resolved. Also a weak band was observed at 932 cm^{-1}, which had been observed earlier. The spectra of the reaction products in all of these mixed fluorine/chlorine experiments are shown in Figure 2. Band positions are listed in Table I.

CsCl + $SiCl_4$. The perchloro reaction mixture of CsCl with Ar/$SiCl_4$ was investigated in one experiment, and despite a full deposition period, no bands were detected which could be attributed to a reaction product. A weak band was observed at 460 cm^{-1} which has been ascribed to the reaction product of CsCl with residual H_2O, indicating that CsCl was indeed present.[11]

KCl + $SiCl_4$. This reaction mixture was investigated in two experiments, and like the Cs analogue, no reaction products were observed, despite a full 24-h deposition, with M/R values of 400 and 150.

Discussion

The reaction of CsF with SiF_4 in argon matrices gave rise to a total of six product bands, demonstrating that a distinct reaction had occurred. In the several experiments carried out with these reactants, over a large range of concentrations, all six bands showed constant relative intensities, indicating that a single product species was being formed. Moreover, the product bands persisted at dilutions as high as M/R = 1000, suggesting a 1:1 complex was formed. This is further substantiated by the fact that the known 2:1 product Cs_2SiF_6 was not observed during initial deposition. When the matrix was thoroughly annealed to allow complete diffusion, an intense band characteristic of SiF_6^{2-} did grow in, suggesting that the initial product species was intermediate between SiF_4 and the final stable SiF_6^{2-} species. Moreover, switching from CsF to KF had very little effect on the overall spectrum, with each product band shifting 0–3 cm^{-1}. In view of the stability of the SiF_5^- anion and its previous synthesis in crystals, the known products in other salt/molecule matrix reactions, the known stability of GeF_5^- and SnF_5^-, and the evidence outlined above, the assignment of the product species in these experiments to the SiF_5^- anion in the $M^+SiF_5^-$ ion pair is made. Certainly, the stretching bands are in the correct region of the spectrum, below the parent SiF_4 and also below the isoelectronic PF_5, which should be more strongly bound due to the additional nuclear charge on the P atom. In addition, the stretching bands observed here between 800 and 950 cm^{-1} are in the same region as the rather broad bands observed by earlier workers who studied SiF_5^- in crystalline environments.[6,7]

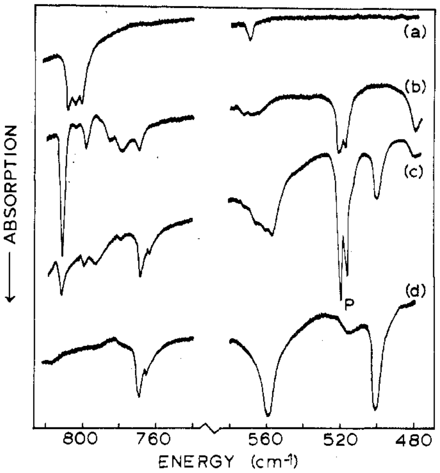

Figure 2. Infrared spectra of the reaction products involving mixed fluorine/chlorine samples. Trace (a) shows the product bands from the reaction of CsCl with Ar/SiF_4. Trace (b) shows the spectra of the reaction products of CsF with a sample of Ar/(SiF_4, $SiClF_3$, $SiCl_2F_2$, $SiCl_3F$, and $SiCl_4$), with the more highly fluorinated species being dominant. Trace (c) shows the spectrum of the reaction of CsF with a similar gas sample but with the more highly chlorinated species dominant. Trace (d) shows the spectrum of the reaction products of CsF with Ar/$SiCl_4$, over selected spectral regions.

The reaction product of CsCl with SiF_4 can be assigned in a similar fashion to the $M^+SiClF_4^-$ ion pair, with several bands in the Si–F stretching region above 800 cm^{-1} and a new band at 570 cm^{-1}, indicative of a Si–Cl stretching vibration. Likewise, the reaction of CsF with $SiCl_4$ showed three bands, two in the Si–Cl stretching region and one at 769 cm^{-1} in the Si–F stretching region, all assigned to the $Cs^+SiCl_4F^-$ ion pair.

The spectra of the completely mixed halogen experiments are much less easily interpreted, due to the number of both parent and product bands observed in each experiment. However, certain patterns and series were observed throughout. The band observed at 812 cm^{-1} shifted to slightly lower energy as each fluorine was replaced in turn by a chlorine atom, until the $SiCl_4F^-$ anion was formed with its Si–F stretch at 769 cm^{-1}. The intermediate band positions were approximately 802, 787, and 779 cm^{-1} for the mono-, di-, and trisubstituted anion. Since this band sequence was observed for all of the product species, including the $SiCl_4F^-$ anion, it can be assigned to the last fluorine to be replaced. (The structure of the anion will be discussed in a later section in this paper.)

The band at 932 cm^{-1} in the SiF_5^- spectrum also had a number of analogous bands in the mixed halogen experiments, at 932, 928, and 925 cm^{-1}, corresponding to the mono-, di-,

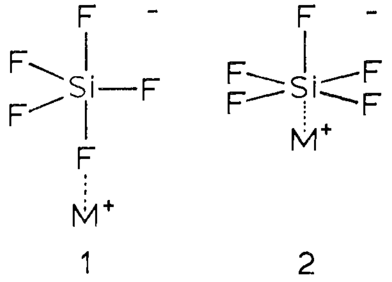

Figure 3. Two possible geometries for the $M^+SiF_5^-$ ion pair isolated in an argon matrix.

and trichlorinated species. However, no analogue was observed in the CsF + $SiCl_4$ reaction, indicating that this vibration transforms into a Si–Cl stretch in the $SiCl_4F^-$ species. Consequently, this vibration can be assigned to the next-to-last fluorine to be replaced by a chlorine. Similar band sequences can be observed near 560–570 cm^{-1} for Si–Cl stretches as more chlorines are added to the anion. Band positions and assignments are listed in Table I.

Sufficient spectral evidence is available to make some definitive conclusions concerning the structure of the anion in the ion pair. On the basis of analogy to the isoelectronic PF_5 and normal valence bond considerations, a trigonal-bipyramidal structure is anticipated for the anion. It has also been shown for small anions formed through the salt/molecule reaction technique in matrices that the metal cation has very little effect on the spectrum of the anion. However, the spectrum of the SiF_5^- anion obtained here in an ion pair cannot be explained on the basis of a trigonal-bipyramidal D_{3h} geometry. Such a geometry would predict only two Si–F stretching vibrations, while three were observed.[13] Moreover, the D_{3h} structure predicts three Si–F deformation modes, two in the region 400–500 cm^{-1} and one below 300 cm^{-1}. Instead, three bands were observed in the 400–500 cm^{-1} region. These observations rule strongly against a D_{3h} geometry for the SiF_5^- anion in the ion pair.

A more appropriate structure for this ion pair might well be a trigonal-bipyramidal structure for the anion, perturbed in some fashion by the alkali metal cation, so that the symmetry of the anion is reduced and more vibrations are activated, as shown in structure 1 of Figure 3. A model for this interaction might well be the $M^+Mn(CO)_5^-$ ion pair, which has been studied in solution, both as solvent-separated ion pair and as a contact ion pair, such as might be anticipated in an argon matrix.[14] The $Mn(CO)_5^-$ anion has been assigned a D_{3h} geometry in the solvent-separated ion pair, while the spectrum of the anion in the contact ion pair is consistent with a C_{3v} geometry with an axial interaction with the alkali metal cation. This spectrum shows exactly three carbonyl stretching vibrations, similar to the three bands observed here for the SiF_5^- anion, with the relative intensities of the three bands matching very closely the intensities observed here. This suggests that an analogous structure might be found in the $M^+SiF_5^-$ ion pair.

In a C_{3v} geometry not three but rather four stretching bands are anticipated. However, Edgell[15] and others[16] have shown that to first order not all bands are activated under such a perturbation. Using Edgell's theory of dual symmetry, one predicts only three stretching bands, not the four anticipated under strictly C_{3v} symmetry. Physically, this is interpreted by observing that the three equatorial fluorines are still very close to planar, and consequently the symmetric stretch of the equatorial fluorines will be very weak and not observed. The three anticipated bands are due to the antisymmetric stretch of the equatorial fluorines, the axial stretch of the bridging fluorine, and the axial stretching of the nonbridging fluorine. These are precisely the assignments made for the $M^+Mn(CO)_5^-$ anion, and similar assignments are made here. This scheme assigns the band at 855 cm^{-1} to the doubly degenerate equatorial antisymmetric stretching mode, which is consistent with that fact that this band disappeared as soon as one chlorine was substituted (and weak bands appeared at 902 and 879 cm^{-1}), since all prior evidence suggests that the chlorine will occupy an equatorial position. This scheme assigns the upper band, at 932 cm^{-1}, to the nonbridging fluorine, which is consistent with the fact that it was the next to last fluorine to be replaced by a chlorine. Finally, the band at 812 cm^{-1} is assigned to the bridging fluorine immediately adjacent to the metal cation. This interaction should elongate this Si–F bond and consequently lower the stretching frequency somewhat, as is generally observed for bridging carbonyl ligands. Moreover, this band persisted with only slight shifts to lower energy as chlorines were added to the anion, consistent with the fact that this vibration is assigned to an axial fluorine. The model of an axial perturbation by the alkali metal cation is consistent with all of the spectral features of the $M^+SiF_5^-$ ion pair and the observed band behavior as chlorine substitution is effected. Moreover, the model of the $M^+Mn(CO)_5^-$ ion pair seems to hold quite well here.

Two other geometries must be considered for this ion pair as well. The first is a C_{4v} square-pyramidal arrangement for the SiF_5^- anion, with the M^+ cation sitting at the base of the pyramid, as depicted in structure 2 of Figure 3. The anticipated spectrum for such a structure does predict three Si–F stretching frequencies, as is observed. Moreover, this structure is known to be an intermediate in a Berry pseudorotation, so it must be energetically only slightly higher in energy. However, this structure cannot readily account for the substitution behavior when chlorine atoms are added. Also, other studies have shown that a monodentate arrangement is usually preferred in these complexes.[17-19] Nonetheless, the C_{4v} structure cannot be ruled out.

A second possible configuration is a C_{2v} structure with a monodentate, equatorial M^+–F interaction. This structure predicts a total of five Si–F stretching vibrations, but if two were very weak, then the pattern of three Si–F stretching bands might be observed. However, this interaction infers, as chlorine atoms are added, that an F atom stays in the equatorial position in $SiCl_4F^-$, although the F is anticipated, by analogy to PCl_4F, to be in the axial position.[20] The fact that only three bands were observed, in conjunction with the axial preferences of fluorine atoms in similar structures, suggests that the C_{2v} structure is less likely, although it cannot be eliminated on the basis of the present evidence.

It is noteworthy that attempts to form the $M^+SiCl_5^-$ ion pair were not successful, even though synthesis of the $M^+SiCl_4F^-$ ion pair was achieved. This result must be attributed to the size of the Cl^- entity, and the relatively small silicon center. While the PCl_5 species is known, it is very unstable, and the $SiCl_5^-$ anion is expected to be even less stable. This result sheds some doubt on the previously reported synthesis of $SiCl_5^-$ in a crystalline environment,[21] but this very different environment may serve to stabilize the $SiCl_5^-$ anion.

The results obtained in this study verify earlier evidence that five-coordinate silicon anions are relatively stable species, especially with fluorine ligands, so that it is quite likely that they do serve as intermediates in organosilicon reactions. While these reactions do involve alkylsilicon compounds and F^-, by analogy with SiF_5^- those species should be relatively stable, and further studies directed at these species are in progress.

Conclusions

The salt/molecule reaction technique has been used in conjunction with the matrix isolation technique to synthesize the $M^+SiF_5^-$ ion pairs for two different alkali metal cations. Three Si–F stretching bands were observed, as well as three deformation modes. The results are consistent with a trigonal-bipyramidal geometry for the anion in the ion pair and a monodentate, axial interaction between the cation and anion, although the C_{2v} and C_{4v} structures cannot be ruled out. The synthesis of the mixed chlorine/fluorine species was also carried out, for all combinations of Cl and F. However, all attempts to synthesize the $SiCl_5^-$ ion were unsuccessful, presumably due to the size of the chloride ligand. The results also indicate that five-coordinate silicon anions are quite stable entities and may well be the active intermediates in those organosilicon reactions where the fluoride anion F^- is used as a catalyst.

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Registry No. $Cs^+SiF_5^-$, 71661-67-1; $Cs^+SiClF_4^-$, 71697-69-3; $Cs^+SiCl_2F_3^-$, 71661-68-2; $Cs^+SiCl_3F_2^-$, 71661-69-3; $Cs^+SiCl_4F^-$, 71697-70-6; SiF_4, 7783-61-1; $SiCl_4$, 10026-04-7; $SiClF_3$, 14049-36-6; $SiCl_2F_2$, 18356-71-3; $SiCl_3F$, 14965-52-7; CsF, 13400-13-0; KF, 7789-23-3; CsCl, 7647-17-8.

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Group 3A and 4A Substituted AB$_5$ Hydrides

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Crystallographic cell volume data are presented for a series of alloys $LaNi_{5-x}M_x$ (M = Al, Ga, In, Si, Ge, Sn) for x = 0–0.5. Pressure–composition desorption isotherms were measured for the hydrides of $LaNi_{4.6}Si_{0.4}$ and $LaNi_{4.6}Ge_{0.4}$ at 30, 40, and 60 °C. From plots of ln P vs. $1/T$ the enthalpies and entropies of transition were calculated to be −8.5 kcal/mol of H_2 and −27.3 cal/(mol of H_2 deg) for $LaNi_{4.6}Si_{0.4}H_y$ and −8.2 kcal/mol of H_2 and −26.5 cal/(mol of H_2 deg) for $LaNi_{4.6}Ge_{0.4}H_y$. The thermodynamic quantities as well as the hysteresis behavior of these hydrides are compared to data previously obtained for the hydrides of $LaNi_{4.6}Al_{0.4}$, $LaNi_{4.6}Ga_{0.4}$, $LaNi_{4.6}In_{0.4}$, and $LaNi_{4.6}Sn_{0.4}$.

Alloys with the $CaCu_5$ structure have been extensively studied because of their ability to absorb and desorb large quantities of hydrogen gas rapidly.[1b] It has recently been observed that relatively small mole fractions of a third element, for example Al, when substituted for Ni, can have a large effect on the hydrogen dissociation pressure of the corresponding hydride.[2-5] Decomposition isotherms for the series of alloy hydrides $LaNi_{4.6}M_{0.4}H_y$ (M = Al, Ga, In, Sn) have been published elsewhere.[6,7] We now wish to report cell volume data for the alloy series $LaNi_{5-x}Ga_x$ (x = 0–0.5), $LaNi_{5-x}In_x$ (x = 0–0.5), $LaNi_{5-x}Si_x$ (x = 0–0.5), $LaNi_{5-x}Ge_x$ (x = 0–0.5), and $LaNi_{5-x}Sn_x$ (x = 0–0.5) and pressure–composition isotherms for the hydrides $LaNi_{4.6}Si_{0.4}H_y$ and $LaNi_{4.6}Ge_{0.4}H_y$.

Experimental Section

Alloys were prepared by using standard arc-melting techniques under an atmosphere of argon. Alloy lattice parameters were determined from X-ray powder diffraction photographs using filtered Fe Kα radiation. A least-squares computer program was used to obtain the final lattice parameters. The procedure for measuring pressure–composition desorption isotherms of the hydrides was identical with that described previously.[2]

Results and Discussion

Plots of the crystallographic unit cell volume, v, vs. the mole fraction x, of the group 3A and 4A element substituents are given in Figure 1a for all six ternary alloys. A more detailed crystallographic analysis will be published elsewhere.[8] Desorption isotherms for the hydrides $LaNi_{4.6}Si_{0.4}H_y$ and $LaNi_{4.6}Ge_{0.4}H_y$ are shown in Figure 2 for temperatures of 30 and 60 °C. Isotherms were also obtained at 40 °C but are not shown. Table I lists thermodynamic data obtained for the hydrides $LaNi_{4.6}M_{0.4}H_y$ (M = Al, Ga, In, Si, Ge, Sn) from plots of log $P_{plateau}$ vs. $1/T$. The pressures used in the van't Hoff plots were taken near the middle of the two-phase plateau

Table I. Thermodynamic and Cell Volume Data for 3A and 4A Substituted $LaNi_5$ Alloys

alloy	$\Delta H_{\alpha\to\beta}$, kcal/mol of H_2	$\Delta S_{\alpha\to\beta}$, cal/(deg mol of H_2)	ΔG,[b] kcal/mol	cell vol, Å^3
$LaNi_{4.6}Al_{0.4}$	−8.7	−26.1	−1.05	87.9
$LaNi_{4.6}Ga_{0.4}$	−8.4[a]		−0.7	88.1
$LaNi_{4.6}In_{0.4}$	−9.5	−26.5	−1.7	91.0
$LaNi_{4.6}Si_{0.4}$	−8.5	−27.3	−0.5	86.9
$LaNi_{4.6}Ge_{0.4}$	−8.2	−26.5	−0.4	87.8
$LaNi_{4.6}Sn_{0.4}$	−9.2	−26.2	−1.5	91.0

[a] Calculated from a single desorption isotherm assuming a value of −26.3 for $\Delta S_{\alpha\to\beta}$. [b] Calculated for 20 °C.

Table II

alloy	temp, °C	H atoms/mol of alloy[a] (β phase)
$LaNi_{4.6}Al_{0.4}$	30	4.7
$LaNi_{4.6}Ga_{0.4}$	22	4.5
$LaNi_{4.6}In_{0.4}$	30	4.6
$LaNi_{4.6}Si_{0.4}$	30	3.5
$LaNi_{4.6}Ge_{0.4}$	30	4.0
$LaNi_{4.6}Sn_{0.4}$	30	4.2

[a] Values obtained by a visual estimate of the two-phase plateau region and β-phase boundary.

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