cess TiO_2 was filtered from the solution before making the nmr measurements.

In contrast to the report of Caglioti and co-workers[2] and in agreement with Schmitt, *et al.*,[3] we find that the TiF_6^{2-} ion is very stable in water. Over long periods of time only a sharp singlet is seen in the F^{19} nmr spectrum of the solution at room temperature. $(NH_4)_2TiF_6$ in a 10% HCl solution was prepared and examined by nmr spectroscopy. The spectrum showed the presence of $TiF_5 \cdot H_2O^-$ and TiF_6^{2-}. These species were in a 2:3 ratio. The formation of $TiF_5 \cdot H_2O^-$ is suggested to occur by the mechanism

$$TiF_6^{2-} + H_3O^+ \overset{\text{fast}}{\rightleftharpoons} F_5TiFH^- + H_2O$$

$$F_5TiFH^- + H_2O \xrightarrow{\text{slow}} F_5TiH_2O^- + HF$$

For TiF_6^{2-} to hydrolyze in water, an acid solution is required, because the formation of a hydrogen bond and subsequent formation of HF helps to break the Ti–F bond.

This result is consistent with the reported acid-catalyzed fluorine exchange between SiF_6^{2-} species.[12] These results are also in agreement with the proposed mechanism for the acid-catalyzed hydrolysis of *trans*-$Co(en)_2F_2^+$ where the formation of a hydrogen bond to fluorine weakens the Co–F bond.[13]

In Figure 3 the $TiF_5 \cdot H_2O^-$ doublet for an initial $HF:TiF_4$ ratio of 1:1 is compared to the doublet for an initial $HF:TiF_4$ ratio of 2:1. Exchange is much faster in the more acidic solution. We suggest that the exchange is due to exchange of both water and fluoride ion. The fluoride ion exchange is facilitated in more acidic solutions by the initial formation of a hydrogen bond, thus lending additional support for the mechanism proposed above.

Acknowledgment.—Support of this work by the Air Force, Materials Laboratory, Research and Technology Division, Wright-Patterson AFB, Ohio, is gratefully acknowledged.

(12) E. L. Muetterties and W. D. Phillips, *J. Am. Chem. Soc.*, **81**, 1084 (1959).

(13) F. Basolo, W. R. Matoush, and R. G. Pearson, *ibid.*, **78**, 4883 (1956)

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Vibrational Frequencies and Force Constants of Some Group IVa and Group Va Hexafluoride Ions[1]

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Infrared and Raman spectral data are reported for crystalline salts containing the ions PF_6^-, AsF_6^-, SbF_6^-, SiF_6^{2-}, GeF_6^{2-}, and SnF_6^{2-}. Five of the six fundamental vibrational frequencies of each ion were assigned on the basis of an O_h structure, and simple valence force constants were calculated.

Introduction

Incomplete infrared and Raman spectral data are available in the literature on a number of crystalline hexafluoride ions of group IVa and group Va metals. Since spectral data on solid substances are harder to obtain and more likely to be ambiguous than similar data for liquids and gases, this field has been largely neglected. However, by careful design of the sample cells, we obtained rather good Raman spectra of the hexafluoride ions of P, As, Sb, Si, Ge, and Sn. Infrared spectra of these compounds were also secured.

Experimental Section

Baker and Adamson reagent grade Na_2SiF_6 was further purified by recrystallization from aqueous HF solution. To prepare K_2GeF_6, GeO_2 (Fischer Scientific Co.) was heated with 48% HF for several days. The filtrate was diluted to 500 ml and the pH was adjusted to 1.5 with KOH. The crystals of K_2GeF_6, which formed after evaporation at room temperature, were filtered and dried in a stream of nitrogen. Na_2SnF_6 was prepared by adding 48% aqueous HF to an aqueous solution of $Na_2SnO_3 \cdot 3H_2O$ (Baker and Adamson) until all of the initially precipitated SnO_2 redissolved. The solution was allowed to evaporate slowly and the crystals were dried with a stream of nitrogen. The KPF_6 was Matheson Coleman and Bell material, 98–100% pure. $CsAsF_6$ was obtained by dissolving CsF in 48% aqueous HF. AsF_5 gas (Ozark Mahoning Co.), diluted with nitrogen, was passed through the solution until no further precipitate was formed. The solid $CsAsF_6$ precipitate was washed with 48% HF and vacuum dried. $LiSbF_6$ was formed from dry LiF in a Kel-F reactor attached to a metal vacuum system. Anhydrous HF was added to the LiF with stirring, and purified SbF_5 was then slowly condensed into the reactor. The products were removed from the vacuum line and dissolved in anhydrous HF from which $LiSbF_6$ was obtained by fractional crystallization. Inert polyethylene and Kel-F containers were used for all preparations.

The Raman spectra of the solid powders were observed by means of a Cary Model 81 Raman spectrophotometer. Samples were contained in conical quartz tubes. Tapered conical sample tubes for solids are described by Brandmüller and Moser.[2] Our tubes were similar to that pictured by Busey and Keller.[3]

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(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

(2) J. Brandmüller and H. Moser, "Einführung in die Ramanspektroskopie," Dr. Dietrich Steinkopff Verlag, Darmstadt, Germany, 1962, p 290.

(3) R. H. Busey and O. L. Keller, Jr., *J. Chem. Phys.*, **41**, 216 (1964).

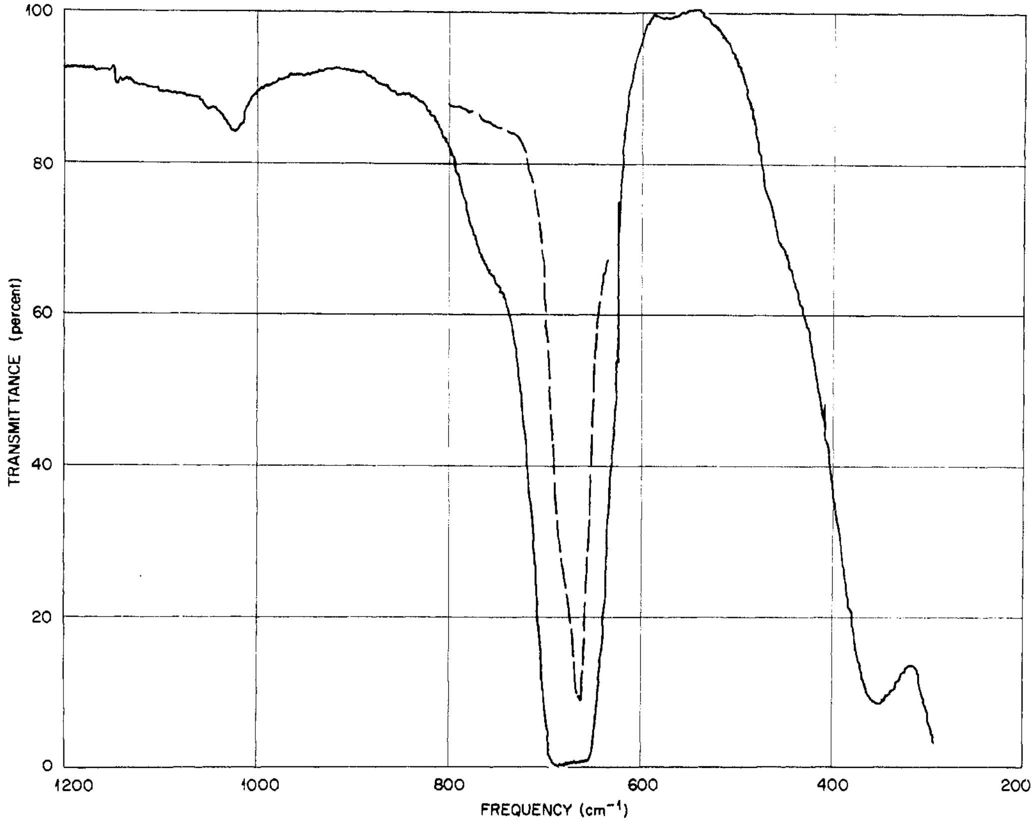

Figure 1.—Infrared spectrum of solid $LiSbF_6$; KBr pellet; Perkin-Elmer 521 spectrometer.

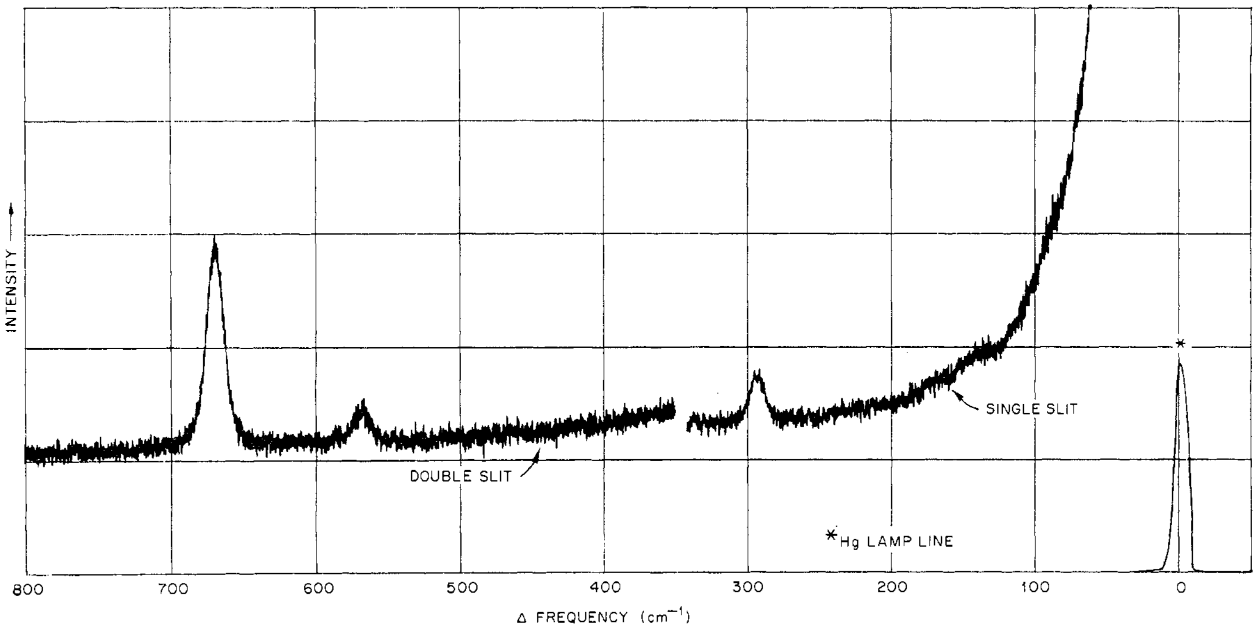

Figure 2.—Raman spectrum of solid $LiSbF_6$; tapered quartz cell; Cary Model 81 spectrophotometer.

They were, however, fabricated from quartz which resisted corrosion from HF slightly better than Pyrex. The 4358-A exciting line was filtered through an n-propyl alcohol solution of ethyl violet and Cyasorb UV24 (American Cyanamid Co.). The infrared spectra were recorded from 250 to 4000 cm^{-1} with a Perkin-Elmer Model 521, double-beam, grating spectrophotometer. Most of the infrared data were obtained with pellets formed from powdered mixtures of each salt wih KBr, but runs on mineral oil mulls or dry powders usually were made to check the results.

Results

Typical infrared and Raman spectra are shown in Figures 1–3. In all cases, three Raman peaks and two infrared bands were observed. In some cases the low-energy infrared absorption band was split, and the high-energy infrared absorption band tended to show shoulders or asymmetry on the high-frequency side. The experimental results are given in Table I, along with

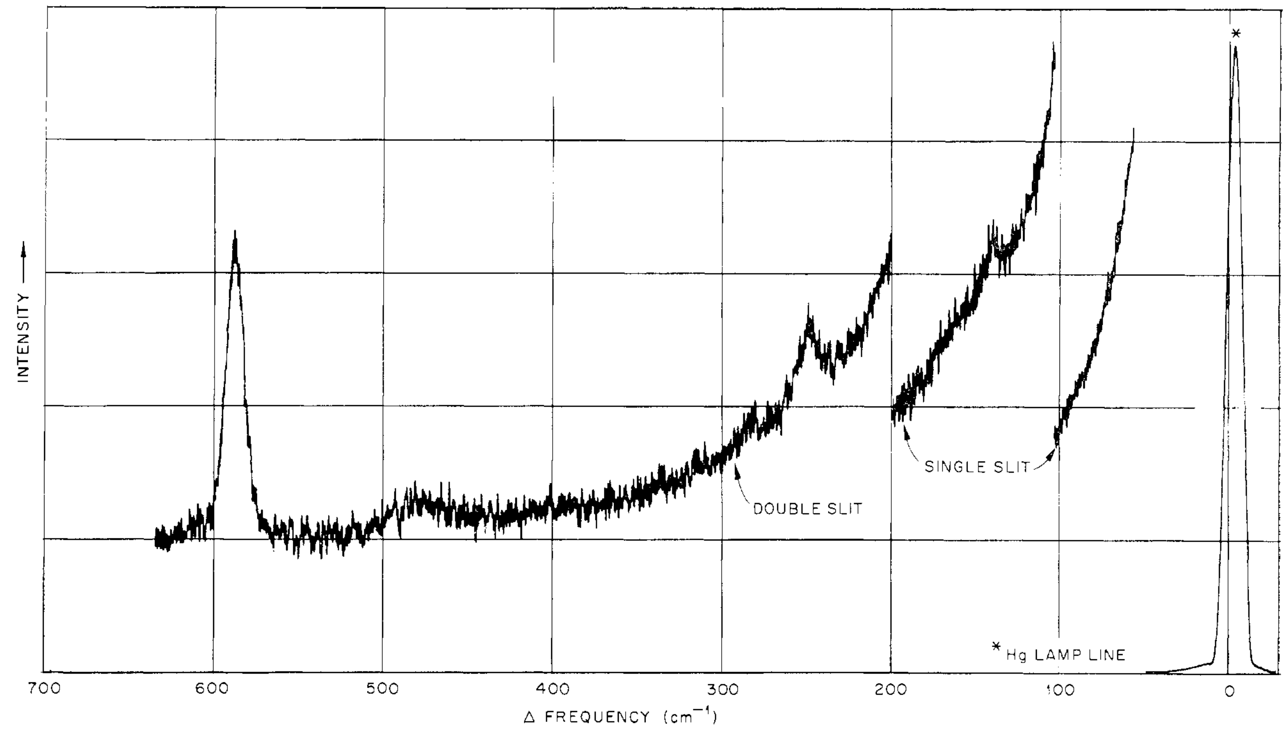

Figure 3.—Raman spectrum of solid Na_2SnF_6; tapered quartz cell; Cary Model 81 spectrophotometer.

Table I

Vibrational Frequencies of Some Group IVa and Group Va Hexafluoride Ions (cm^{-1})[a]

Compound (solid)	Raman			Infrared	
	ν_1 (A_{1g})	ν_2 (E_g)	ν_5 (F_{2g})	ν_3 (F_{1u})	ν_4 (F_{1u})
KPF_6	751 (10) [741]^b	580 (2.2)	477 (3.7)	830 s	558 m
$CsAsF_6$	685 (10)	576 (2.3)	372 (2.6)	699 s	392 m
$LiSbF_6$	668 (10)	558 (2.1)	294 (4.4)	669 s	350 m
Na_2SiF_6	663 (10) [646]^g [655]^h [656]^d [649]^f	477 (3.5) [466]^g [474]^h [465]^d	408 (2.9) [403]^g [395]^h [395–400]^d	741 s [741]^h [740]^d	483 m [476]^h [485]^d
K_2GeF_6	624 (10) [627]^c [613]^i	471 (1.6) [454]^c	335 (3.5) [318]^c[326]^i	603 s [600]^e[605]^c	359 m, 339 m [350]^e [335], 356]^c
Na_2SnF_6	592 (10) [593]^l [585]^j [572]^k	477 (1.0) [620]^l [470]^j [460]^k	252 (1.6) [342]^l [241]^j [247]^k	559 s [564]^l	300 m

[a] s, strong; m, medium. Numbers in parentheses are relative Raman intensities. Numbers in brackets are literature values. Unless it is specifically noted otherwise, all data refer to the solid state. [b] L. A. Woodward and L. E. Anderson, *J. Inorg. Nucl. Chem.*, **3**, 326 (1956) (NH_4PF_6 in aqueous solution). [c] J. E. Griffiths and D. E. Irish, *Inorg. Chem.*, **3**, 1134 (1964) (infrared, various GeF_6^{2-} salts; Raman, H_2GeF_6 in aqueous solution). [d] R. B. Badachhape, G. Hunter, L. D. McCory, and J. L. Margrave, *ibid.*, **5**, 929 (1966) (various SiF_6^{2-} compounds; Raman values in aqueous solution). [e] D. H. Brown, K. R. Dixon, C. M. Livingston, R. H. Nuttall, and D. W. A. Sharp, *J. Chem. Soc., Sect. A*, 100 (1967). [f] Y. K. Syrkin and M. V. Wolkenstein, *Acta Physicochim. URSS*, **2**, 308 (1935) (H_2SiF_6 in aqueous solution). [g] L. Couture-Mathieu and J. P. Mathieu, *J. Chim. Phys.*, **49**, 226 (1952) ($(NH_4)_2SiF_6$). [h] P. A. W. Dean and D. F. Evans, *J. Chem. Soc., Sect. A*, 698 (1967) (infrared, Cs_2SiF_6; Raman, $(NH_4)_2SiF_6$ in aqueous solution). [i] See footnote *h* (Cs_2GeF_6). [j] See footnote *h* ($(NH_4)SnF_6$ in aqueous solution). [k] See footnote *h* (Cs_2SnF_6). [l] H. Kriegsmann and G. Kessler, *Naturwissenschaften*, **47**, 393 (1960) ($K_2SnF_6 \cdot H_2O$ and $(NH_4)_2SnF_6$).

values from the literature if these were available. Literature values for aqueous solutions of the ions are also included in the table. In Table I we assumed the ions have simple O_h structures and made assignments of the fundamental vibrational frequencies on that basis.

Discussion

The major features of the Raman and infrared spectra are accounted for by assuming octahedral structures (O_h) for the anions. For this configuration, we expect three Raman-active fundamental vibrations, ν_1, ν_2 (double degenerate), and ν_5. Two infrared-active vibrations, ν_3 and ν_4 (both triple degenerate), should be observed. The sixth vibration, ν_6, is inactive in both the infrared and Raman spectra. X-Ray studies of the crystalline compounds are summarized in Table II. These studies support the spectral conclusion that the configurations of the anions are close to octahedral.

The site symmetries of the anions are listed in Table II. In general, these symmetries are lower than the group symmetry which is close to O_h in all cases. If we use a simple site-group analysis, such as that suggested

TABLE II

CRYSTAL SYMMETRY OF HEXAFLUORIDE COMPOUNDS

Compound	Space group	Group symmetry	Central ion site symmetry	M–F distance, A	Ref
KPF_6	Fm3m	O_h	O_h	1.58	*b*
$CsAsF_6$	$R\bar{3}$	$O_h{}^a$	S_6	1.82^h	*c*
$LiSbF_6$	$R\bar{3}$	O_h	S_6	1.877	*d*
Na_2SiF_6	P321	$O_h{}^a$	C_3, D_3	1.695	*e*
K_2GeF_6	$P\bar{3}m1$	$O_h{}^a$	D_{3d}	1.76	*f*
Na_2SnF_6	Immm	$O_h{}^a$	D_{2h}	2.05	*g*

[a] Possibly some distortion present. [b] H. Bode and H. Clausen, *Z. Anorg. Allgem. Chem.*, **265**, 229 (1951). [c] B. Cox, *J. Chem. Soc.*, 876 (1956). [d] J. H. Burns, *Acta Cryst.*, **15**, 1098 (1962). [e] A. Zalkin, J. D. Forrester, and D. H. Templeton, *ibid.*, **17**, 1408 (1964). [f] J. L. Hoard and W. D. Vincent, *J. Am. Chem. Soc.*, **61**, 2849 (1939). [g] D. H. Brown, K. R. Dixon, R. D. W. Kemmitt, and D. W. A. Sharp, *J. Chem. Soc.*, 1559 (1965). [h] R. D. W. Kemmitt, D. R. Russell, and D. W. A. Sharp, *ibid.*, 4408 (1963).

by Halford,[4] we would expect degenerate vibrations in the crystals to be split and selection rules to be relaxed. The correlation tables may be used to predict specifically which bands may split or change activity. A number of the infrared spectra showed shoulders or irregular peaks which indicated these effects. However, most of the influences of site symmetry must be second order since the great majority of the possible splittings and selection rule relaxations were not observed in our spectra. Some of these effects could possibly be observed if better spectra were obtainable. A very definite splitting of the ν_4 frequency in K_2GeF_6 occurs, which is in accord with the symmetry of the $GeF_6{}^{2-}$ ion site in the crystal. This effect has been observed in $GeF_6{}^{2-}$ by Griffiths and Irish.[5] The frequency ν_6 which is inactive in the O_h structure should become infrared active in all of the lower symmetries. The expected frequencies, however, would be in the range 200–400 cm^{-1}. The long-wavelength limit of our infrared spectrophotometer was 250 cm^{-1} and the window materials made observations below 350 cm^{-1} difficult, so no bands were observed which could be attributed to ν_6. The two combination bands, $\nu_5 + \nu_6$ and $\nu_2 + \nu_6$, should be active in the infrared spectra of these compounds, and these bands often provide a means of determining ν_6. Shoulders in the infrared spectra were observed in the region of the ν_3 band in nearly all of the spectra. However, these were not sufficiently resolved or reproducible to permit assignments of combination bands.

Light-scattering effects produced some variations of the spectra in the pellets, although the main band centers were relatively constant. Spectra from mulled samples tended to be poorly resolved with broad bands. Three infrared absorption bands were observed near ν_1 with pellets made from KPF_6 and KBr. With mineral-oil mulls, KPF_6 gave one broad absorption band with shoulders on the short-wavelength side. It was not clear whether the splitting in the pellet was due to resolution of combination bands or to exchange effects between KPF_6 and KBr. Because of this uncertainty, we have reported only data obtained from mineral-oil mulls of KPF_6.

Force Constant Calculation

A number of force constant treatments of six-atom octahedral molecules have been published.[6-8] Following Claassen[6] and Pistorius,[7] we have used a simple valence force treatment of the hexafluoride ions. The following symmetry coordinates were used.

$$S_1(a_{1g}) = 1/\sqrt{6}(\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4 + \Delta r_5 + \Delta r_6)$$

$$S_2(e_g) = 1/\sqrt{12}(\Delta r_1 - 2\Delta r_2 + \Delta r_3 + \Delta r_4 - 2\Delta r_5 + \Delta r_6)$$

$$S_3(f_{1u}) = 1/\sqrt{2}(\Delta r_4 - \Delta r_1)$$

$$S_4(f_{1u}) = 1/\sqrt{8}(\Delta\alpha_{24} + \Delta\alpha_{34} + \Delta\alpha_{45} + \Delta\alpha_{46} - \Delta\alpha_{12} - \Delta\alpha_{13} - \Delta\alpha_{15} - \Delta\alpha_{16})$$

$$S_5(f_{2g}) = 1/2(\Delta\alpha_{23} + \Delta\alpha_{56} - \Delta\alpha_{26} - \Delta\alpha_{35})$$

$$S_6(f_{2u}) = 1/\sqrt{8}(-\Delta\alpha_{24} + \Delta\alpha_{34} - \Delta\alpha_{45} + \Delta\alpha_{46} + \Delta\alpha_{12} - \Delta\alpha_{13} + \Delta\alpha_{15} - \Delta\alpha_{16})$$

Here r_1, r_2, etc., are the distances from the central atom to the fluorine atoms, and α_{12} is the angle F_1–M–F_2, etc. The fluorine atoms are numbered counterclockwise, looking down on the common plane of F_2, F_3, F_5, and F_6 with F_1 above and F_4 below the plane, respectively. All the α's were taken as 90°. The metal–fluorine distances were taken to be equal in each molecular ion, and the values used are listed in Table II. Since only five frequencies were observed for each molecule, we simplified the force constant matrix and included only the following valence force constants: f_r, the bond stretching constant for the metal–fluorine bond; $f_{rr'}$, the constant for interaction between a bond being stretched and the bond opposite to it; f_{rr}, the constant for interaction between a bond being stretched and an adjacent bond; f_α, the angle bending constant; and $f_{\alpha\alpha}$, the constant for interaction between an angle and an adjacent angle in the same plane. For the two small ions, $PF_6{}^-$ and $SiF_6{}^{2-}$, no real solutions could be found using only these constants; in these cases, an off-diagonal term, $F_{34} = 2(f_{r\alpha} - f_{r\alpha'})$, was included in the computation. Here $f_{r\alpha}$ is the interaction constant between an angle and one of the bonds forming its sides, and $f_{r\alpha'}$ is the interaction constant between an angle and a bond in its plane but not forming one of its sides. The Wilson *F–G* matrix method was used to solve the equations relating the normal vibrational frequencies of the ions to the valence force constants of the molecular potential function. A machine-iterative, least-squares process similar to that of Overend and Scherer[9] was employed to solve the determinant for the vibrational frequencies. Values for F_{34} were varied systematically, and the associated F_{33} and F_{44} elements were calculated.

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(4) R. S. Halford, *J. Chem. Phys.*, **14**, 8 (1946).

(5) J. E. Griffiths and D. E. Irish, *Inorg. Chem.*, **3**, 1134 (1964).

(6) H. H. Claassen, *J. Chem. Phys.*, **30**, 968 (1959).

(7) C. W. F. T. Pistorius, *ibid.*, **29**, 1328 (1958).

(8) J. W. Linnett and C. J. S. M. Simpson, *Trans. Faraday Soc.*, **55**, 857 (1959).

(9) J. Overend and J. R. Scherer, *J. Chem. Phys.*, **32**, 1289 (1960).

Some selected results of the force constant calculations are summarized in Table III. These are not a unique set of force constants because of the many interactions that were set equal to zero and because of the arbitrary selection of a value for F_{34}. Claassen[6] has suggested using the value of F_{34} which gives a minimum value of F_{44}. However, we see no special need for this selection and have chosen to use the lowest positive value of F_{34} which gives real solutions. In Table III, values calculated for ν_6, assuming $F_{66} = F_{44}$, are also tabulated.

With a few exceptions, there are regular decreases in the force constants with increasing ion size. If pairs of isoelectronic ions are compared, it is apparent that the doubly charged ion has weaker bond-stretching and bond-bending constants than the singly charged ion. For AsF_6^- and GeF_6^{2-}, the values of f_r are lower than expected and the values of $f_{rr'}$ (opposite bond interactions) are higher. Thus it seems that, for these ions in which the fluorine atoms are beginning to overlap, there is interaction between opposite bond stretching motions which decreases the value of f_r and increases that of $f_{rr'}$. This interaction "through" the central metal ion is smaller for both the smaller and the larger ions.

TABLE III

FORCE CONSTANTS FOR HEXAFLUORIDE IONS (MDYNES/A)

Ion	f_r	f_{rr}	$f_{rr'}$	$f\alpha/r_0^2$	$f\alpha\alpha/r_0^2$	$(f_{r\alpha} - f_{r\alpha'})/r_0$[a]	ν_6 (calcd),[b] cm^{-1}
PF_6^-	4.12	0.43	0.50	0.90	0.13	0.32	402
AsF_6^-	3.72	0.26	0.50	0.58	0.10	0.00	322
SbF_6^-	3.83	0.25	0.16	0.48	0.12	0.00	294
SiF_6^{2-}	3.01	0.40	0.33	0.68	0.02	0.24	347
GeF_6^{2-}	2.71	0.31	0.40	0.47	0.08	0.00	289
SnF_6^{2-}	2.77	0.23	0.24	0.36	0.09	0.00	252

[a] Value assumed. [b] Calculated assuming $F_{66} = F_{44}$.

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Magnetic Properties of Intermetallic Compounds between the Lanthanides and Platinum

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The magnetic properties are reported for a series of intermetallic compounds designated by the formula $LnPt_2$ in which Ln represents Pr, Nd, Gd, Tb, Dy, Ho, or Er. All have the C15 ($MgCu_2$) structure. Emphasis was placed on the paramagnetic region. The effective moment (μ_{eff}) for the paramagnetic $LnPt_2$ compounds is fairly close to $g\sqrt{J(J+1)}$, the value for the free tripositive Ln ion. In $GdPt_2$ μ_{eff} exceeds this by about 2%, which is ascribed to conduction electron polarization effects. The measured μ_{eff} values indicate that Pt in the $LnPt_2$ series is nonmagnetic. Curie–Weiss behavior is observed at all temperatures down to the Curie temperature indicating a relatively weak crystal field interaction. The low moment observed for the samples in the ferromagnetic state is ascribed to failure to achieve saturation. All except $PrPt_2$ become ferromagnetic at 4.2°K. $PrPt_2$ may be a Van Vleck paramagnet at this temperature.

I. Introduction

This study is concerned with the series of intermetallic compounds represented by the formula $LnPt_2$, in which Ln is one of the seven lanthanide elements mentioned in the abstract.[2] The magnetic behavior of this group of compounds was studied earlier by Crangle and Ross,[3] but their attention was confined to the ferromagnetic state. Certain of their observations (*vide infra*) have made it desirable to extend the work to include the paramagnetic region. The present study was largely concerned with that aspect of the $LnPt_2$ compounds and in this sense parallels the work of Farrell and Wallace[4] on the isostructural and chemically similar $LnNi_2$ and $LnCo_2$ series.

Ross and Crangle[3] observed that the moment per formula unit of $LnPt_2$ in the ferromagnetic state was consistently less than gJ, the moment of the free tripositive Ln ion. Since the platinum ion is without moment in the element, it is generally assumed to be nonmagnetic in intermetallic compounds. Thus in the $LnPt_2$ compound the lanthanide is regarded as supplying all of the moment. The discrepancy between the measured moment and gJ in all cases except $GdPt_2$ was ascribed by Crangle and Ross to the quenching effect of the crystalline field. For $GdPt_2$ there was a smaller difference which, of course, cannot be ascribed to this effect. Crangle and Ross attributed it to antiferromagnetic spin polarization of the conduction electrons—that is, net spin of the conduction electrons in opposition to the spin associated with the 4f shell of the Gd ion.

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(1) Participant in the United States–Soviet Union Cultural and Education Exchange Program and on leave from the University of Leningrad, USSR.

(2) Sm and Tm, which are usually included in such studies, were omitted because their volatility is such as to render the making of the high-melting platinum compounds very difficult. Eu and Yb are normally divalent in the metallic state and hence were omitted from this study which was concerned with tripositive lanthanides.

(3) J. Crangle and J. W. Ross, "Proceedings of the International Conference on Magnetism at Nottingham," Institute of Physics and the Physical Society, London, 1964, p 240.

(4) J. Farrell and W. E. Wallace, *Inorg. Chem.*, **5**, 105 (1966).