

63-3-3

OFFICE OF NAVAL RESEARCH

Contract Nonr 1834(13)

Task No. NR 051-215

TECHNICAL REPORT NO. 62

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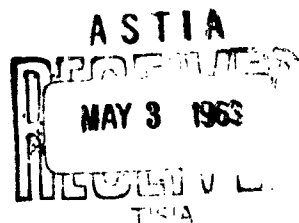
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Prepared for Publication

in the

Journal of Chemical Physics



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March 16, 1963

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AN NMR STUDY OF THE ALKALI HEXAFLUOROPHOSPHATES' DYNAMIC STRUCTURE^{*}

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The fluorine nuclear magnetic resonance spectra of the sodium, potassium, rubidium and cesium hexafluorophosphates were studied between 77°K and 400°K. It was found that in each of the salts the PF_6^- ions are reorienting about the octahedral axes at random or nearly so for temperatures of 200°K and above. The broadening of the fluorine resonance in these solids at lower temperatures indicates that the ease with which the PF_6^- groups reorient increases with increasing size of the alkali metal cation, so that for CsPF_6 the fluorine resonance is still narrow at 77°K. A quantitative study of the potential barriers to PF_6^- group reorientation was discouraged by the discovery that the fluorine line shapes and widths are remarkably sensitive to the physical state and in the case of RbPF_6 the thermal history of the sample. These effects are attributed to crystal imperfections which lower the potential barriers to PF_6^- group reorientations and decrease the size of domains in which there is a cooperative "freezing out" of the reorientations. Thus, in the region of changing line width, we postulate domains with frozen out PF_6^- groups and others with reorienting groups. In samples which should have relatively low imperfection concentrations and where such domains should be large, we find distinguishable broad and narrow components in the fluorine resonance, with one growing at

the expense of the other as the temperature is changed. This two-phase behavior disappears in finely powdered samples, in which high concentrations of imperfections were probably introduced by the mechanical grinding. Fluorine line shape studies reported previously for solid CF_4 are reinterpreted in terms of a similar two-phase, cooperative process for the freezing out of the CF_4 reorientations.

I. INTRODUCTION

These investigations were undertaken to obtain information about the reorientation of octahedral groups in crystalline solids. The alkali hexafluorophosphates, MPF_6 ($M = \text{Na}, \text{K}, \text{Rb}, \text{and Cs}$), were chosen for this study in part because of the favorable nuclear properties of F^{19} but also because all four known alkali hexafluorophosphates crystallize in a sodium chloride type lattice at room temperature. Therefore, differences in behavior of the salts should be governed by the size of the cation. This relative isolation of one factor from the several which affect the dynamic structure of a solid makes these compounds attractive candidates for investigation.

Related NMR studies include that of Murray and Waugh¹ upon the reorientation of the octahedral cobalt(III) hexammine ion in various cobalt(III) hexammine salts. In the chloride, bromide, iodide, and nitrate salts they found two nearly resolved changes in the proton magnetic resonance linewidth, which they attributed to two crystallographically different cobalt hexammine ions in the unit cell. However, because the linewidth changes overlap, they were unable to determine the energy barrier to reorientation of the $\text{Co}(\text{NH}_3)_6^{+3}$ ions in these salts. A single change in the proton linewidth occurred upon cooling $\text{Co}(\text{NH}_3)_6(\text{BF}_4)_3$, from which a barrier height of 12 kcal/mole and an

inverse frequency factor, τ_0 , of 10^{-14} sec were obtained for the reorientation of the $\text{Co}(\text{NH}_3)_6^{3+}$ group. More directly relevant is the work of Lustig,² upon the fluorine magnetic resonance spectra of potassium hexafluorophosphate^{2,3} and some silicon hexafluoride salts.² For these salts he was able to obtain barrier heights and frequency factors for reorientation of the anions. He also examined the spectra of rubidium hexafluorophosphate and cesium hexafluorophosphate. However, the results he obtained for potassium hexafluorophosphate and for rubidium hexafluorophosphate differ rather markedly from those obtained in the present study, apparently because of impurities in his samples.

II. EXPERIMENTAL

Samples of the four alkali hexafluorophosphates were obtained from the Ozark-Mahoning Company. Their analyses of these salts indicated the following purities: NaPF_6 , 98.97% by PF_6^- determination, 99.90% by total fluorine determination; KPF_6 , 99.84% by PF_6^- and by total fluorine determinations; RbPF_6 , 98.6% by total fluorine determination; and CsPF_6 , 101.9% by total fluorine determination. We are indebted to Dr. Wayne E. White for providing the samples and their analyses. All of the salts are pure white except the sodium salt which is a light gray. This color was attributed to slight contamination from the polyethylene containers used in the preparation. There was a faint odor of HF present in the sodium salt so the additional fluorine present in it is probably in the form of HF. The samples were stored in a vacuum dessicator over magnesium perchlorate or sodium hydroxide before use. Sample tubes of 9 mm o.d. were filled to a height of about 4 or 5 cm with the polycrystalline salt. They were then placed on a vacuum line, pumped on for about four hours, and sealed. The pressure in the tubes before sealing was 5 to 10×10^{-5} mm Hg.

The NMR spectrometer and cryostat used were similar to those described previously.⁴ The 6300 gauss permanent magnet of this laboratory was used for F^{19} , P^{31} , and Na^{23} studies. The magnetic field was modulated at 28 cps and phase sensitive detection was employed to record the first derivative of the absorption curves, in field-sweep experiments. The second moments were calculated by numerical integration from the recordings of the first derivative, corrections being made for finite modulation amplitude. The temperature of the samples was measured with a copper-constantan thermocouple placed in a well in the side of the sample tube.

III. RESULTS AND DISCUSSION

In this work, our attention was centered upon the F^{19} NMR line shape and its temperature dependence in the four alkali fluorophosphates. The results and discussion are divided into three main parts: (i) the dynamic state of the PF_6^- ions at room temperature; (ii) the temperature dependence of the PF_6^- group reorientations; and (iii) differences in the dynamic structure of the solids which result from changing the cation. One would expect these differences to depend mainly upon the size of the cation, and this is borne out by some "anomalous" irreversibilities in the thermal behavior, particularly the rubidium salt.

The crystal structures of these salts are important in our studies, so a brief review will be given of them. X-ray powder studies^{5,6,7} show that the sodium, potassium, rubidium, and cesium salts studied here, as well as the ammonium and thallium salts, crystallize in a sodium chloride type lattice at room temperature. In this lattice the cations and the phosphorus atoms occupy the face-centered lattice points. The fluorine atoms could not be located at room temperature, but by super-cooling the room temperature form of the potassium salt (α - KPF_6) to $-44^\circ C$, Bode and Clausen⁵ were able to determine the positions of the fluorine atoms and hence the P-F bond length. The P-F bond

length found was 1.58 Å with no uncertainty quoted. This value is quite reasonable and is close to the value found⁸ in PF_3Cl_2 ($1.59 \pm 0.03\text{Å}$) and in PF_5 ($1.54 \pm 0.03\text{Å}$ and $1.57 \pm 0.02\text{Å}$ from two separate determinations), in which the phosphorus is also in a 5+ state, but admittedly in a different coordination state. Table I gives the unit cell constants found for these salts at room temperature. The first value quoted for each salt is the value used for the calculations performed in these studies. The table includes the ionic radii of the cations,⁹ for comparative purposes.

In the powder photographs of the super-cooled $\alpha\text{-KPF}_6$, Bode and Clausen⁵ found new lines appearing which they attributed to a low-temperature modification of this salt, $\beta\text{-KPF}_6$. They were able to index the lines of the low temperature form on the basis of a trigonally distorted body-centered cubic unit cell ($a = 4.85\text{ Å}$, $\alpha = 94^\circ$) containing one formula unit per unit cell, but a thorough study of this form was not undertaken. No other low temperature x-ray data were found for these salts, and this will limit somewhat the amount of information one can obtain from the temperature dependence studies of the second moment.

A. Dynamic State of the PF_6^- Ions at Room Temperature

Observations and calculation of F^{19} second moment

The second moments of the F^{19} NMR absorption observed for the four fluorophosphates at room temperature and above are given in Table II together with the standard deviation of each value. The fluorine resonance saturates easily in these samples at room temperature and care had to be exercised to avoid saturation, particularly as the temperature was raised. In contrast to the usual behavior, the apparent second moment decreases as the rf power is increased. For this reason, the values given are likely to be somewhat low rather than too high, but they should be within 5% of the true values. In any

Table I. Unit cell constants for the face-centered cubic alkali hexafluorophosphates at room temperature and the ionic diameters of the cations in Angstroms.

	NaPF ₆	KPF ₆	RbPF ₆	CsPF ₆
Cell Constant, <u>a</u>	7.61 ^a	7.71 ^b	7.92 ^c	8.22 ^b
	7.61 ^c	7.75 ^c		8.19 ^c
Ionic Diameter ^d	1.90	2.66	2.96	3.38

^aSee reference 6.

^bSee reference 5.

^cSee reference 7.

^dSee reference 9.

Table II. Second moments of the F^{19} NMR absorption observed in the alkali hexafluorophosphates at 25°C and above.

Compound	Second moment	T	Compound	Second moment	T
NaPF ₆	$1.32 \pm 0.03 \text{ G}^2$	26°C	RbPF ₆	$1.07 \pm 0.04 \text{ G}^2$	25°C
	1.35 ± 0.03	98		$1.05_5 \pm 0.02$	125
KPF ₆	$1.04_5 \pm 0.03$	25	CsPF ₆	0.85 ± 0.04	26
	- -	- -		0.85 ± 0.02	135

case, the F^{19} second moments are much less than the 12.2 G^2 calculated^{10,11} for the intragroup, dipole-dipole broadening of the F^{19} resonance for a rigidly fixed PF_6^- ion, in a crystal powder. This indicates that some motion of the hexafluorophosphate ion is occurring at a rate fast enough to narrow the resonance line. Furthermore, the constancy of the second moments at higher temperatures and the similarity of the values for all four salts, 0.85 G^2 to 1.3 G^2 , indicate that a limiting dynamic state is involved.

The question as to what this dynamic state might be is approached in the usual manner.¹¹ The "effective" second moment¹⁰ produced by the magnetic dipole-dipole interactions is calculated for several models and the results are compared with experiment. These calculations start with Van Vleck's treatment of the second moment for a rigid lattice.^{10,11} The second moment S_1 for the resonance absorption, in a single crystal, of nuclear species i , may be written as

$$S_1 = (3/2)I_i(I_i+1)g_i^2\beta^2N_i^{-1} \sum_{i>j} (3\cos^2\theta_{ij}-1)^2r_{ij}^{-6} \\ + (1/3)\beta^2N_i^{-1} \sum_{i,k} I_k(I_k+1)g_k^2(3\cos^2\theta_{ik}-1)^2r_{ik}^{-6} \quad , \quad (1)$$

where I is the nuclear spin; g the nuclear g -value; β the nuclear magneton; N_i the number of nuclei at resonance; and θ_{ij} is the angle between the internuclear vector r_{ij} and the externally applied magnetic field. The indices i and j refer to the nuclei giving rise to the absorption in question and k to other magnetic nuclei in the crystal.

For polycrystalline samples, the angular factor $(3\cos^2\theta-1)^2$ in Eq. (1) must be averaged over the random spatial orientations. The value for this is $4/5$ which converts Eq. (1) to the form

$$S_1 = (6/5)I_1(I_1+1)g_1^2\beta^2N_1^{-1} \sum_{i>j} r_{ij}^{-6} + (4/15)\beta^2N_1^{-1} \sum_{i,k} I_k(I_k+1)g_k^2r_{ik}^{-6} \quad (2)$$

Equation (2) was used with a P-F bond distance of 1.58 Å to calculate the 12.2 G² second moment given in the first paragraph of this Section for the F¹⁹ resonance of a rigid lattice of isolated PF₆⁻ groups. When a group reorients at a frequency large compared with the linewidth, one can calculate the "effective" second moment¹² of the narrowed line by averaging the terms (3cos²θ-1)r⁻³ in Eq. (1) before squaring and before performing the powder average leading from Eq. (1) to Eq. (2).

Reorientations of PF₆⁻ groups about a single axis

The simplest motions which would narrow the fluorine resonance appreciably are reorientations of the PF₆⁻ groups. The PF₆⁻ group has two-, three-, and four-fold symmetry axes about which rotations might occur, and it is conceivable, but not likely, that the crystal fields could restrict the PF₆⁻ group to rotations about a particular one of these axes. If indeed the rotations were restricted in this manner, the angular dependences of the intragroup dipolar broadening would be reduced by the factor

$$(1/4)(3\cos^2\gamma_{ij}-1)^2, \quad (3)$$

where γ_{ij} is the angle between the internuclear vector r_{ij} and the rotation axis. This formula holds for step-wise reorientations about an n-fold axis with $n \geq 3$ and for classical rotation about any axis.¹¹ For such cases, the resultant intragroup second moment is obtained readily by multiplying each term in Eq. (2) by Eq. (3), using the appropriate γ_{ij} or γ_{ik} .

The values calculated by this procedure for the intragroup, dipolar contributions to the F¹⁹ second moment are 2.48, 2.55, and 2.27 G², respectively, for C₂, C₃, and C₄ rotation. The relative contributions of the F-F and F-P

interactions in the three cases are 2.27 and 0.21, 2.55 and 0.00, and 1.43 and 0.84 G^2 . The C_2 rotation would have to be "classical", i.e. with a constant angular velocity, because $n = 2$; the C_3 and C_4 could be either classical or "jump-type". In any event, all of the predicted second moments are $\sim 2.5 G^2$, which, even without the intergroup contributions, is much too large compared to the experimental values of $\sim 1 G^2$ for the motions to consist only of rotations about one PF_6^- axis.

Random, isotropic reorientations of PF_6^- groups

Reorientation about a single axis does not lower the second moment enough to give agreement with experiment, so we consider next a model in which the PF_6^- groups reorient about different axes at random. The PF_6^- group is not too far from being a sphere, because of its octahedral symmetry and the radii of the phosphorus and fluorine atoms. In the limit of spherical symmetry the groups could experience completely uncorrelated reorientations about any axis at random. This would give an isotropic distribution of orientations and reorientations, in which the internuclear vectors would take on with equal a priori probability all possible angles with respect to the crystal axes. For this model, the $(3\cos^2\theta-1)$ angular dependence averages to zero for the intragroup dipolar broadening and we are left with the intergroup interactions.

McCall and Douglass¹³ and Kroon¹⁴ have shown recently that the intergroup terms $(3\cos^2\theta_{ij}-1)/r_{ij}^3$ for random reorientations are equivalent to the rigid lattice values obtained by placing each nucleus at the center of the sphere over which it moves. Thus, one considers the fluorine atoms to be at the phosphorus lattice points for calculating the intergroup contributions to the second moment. This problem reduces to summing r^{-6} for like and unlike neighbors in a face-centered cubic lattice. These summations have been shown¹⁵ to be $115.6/a^6$ and $422.1/a^6$ for the like and unlike neighbors, respectively,

where a is the unit cell length. This procedure was used to calculate the F-F, F-P and F-M dipolar contributions to S_F , for the hexafluorophosphates of the four alkali metals M. There is in addition a small broadening produced by the electron coupling of the P^{31} and F^{19} nuclei within a PF_6^- group. The contribution to the second moment of this splitting is given by¹⁶

$$S_i = (1/3)I_k(I_k+1) \sum_k J_{ik}^2 \quad (4)$$

In aqueous solutions of KPF_6 , the coupling constant J_{PF} is 705 ± 5 cps, which would contribute 0.008 G^2 to S_F .

The various contributions to S_F , on the basis of the random, isotropic reorientation model, are given in Table III along with the experimental values for comparison. It is seen that the calculated values are somewhat smaller, $\sim 0.05 \text{ G}^2$, than those observed, except for the potassium salt, where they agree within error. The differences in the three cases are large enough to be real. Moreover, the sign of the difference is what one would expect if the motions were not truly isotropic. In turn, it seems reasonable that some orientations of the PF_6^- groups should be more probable than others. Accordingly, we will consider this aspect in some detail, with particular reference to the crystal structures of the salts.

Reorientation of PF_6^- groups about octahedral axes at random

The simplest type of restricted rotation model for the PF_6^- group is a "six-position model", one in which a fluorine atom occupies six relatively localized positions in the crystal lattice. Reorientations would be restricted to rotations about the symmetry axes of the group, at random, with the net effect that each fluorine spends $1/6$ of the time in each position. Actually, the groups would experience more or less complex torsional oscillations as well. However, allowance for the torsional oscillations requires a detailed

Table III. The second moments in Gauss² of the F¹⁹ absorption in the alkali hexafluorophosphates calculated for random reorientations, with spherical symmetry, of the PF₆⁻ groups.

Interaction ^a	NaPF ₆	KPF ₆	RbPF ₆	CsPF ₆
F-F	1.131	1.046	0.890	0.712
F-P	0.016	0.014	0.012	0.010
F-M	0.121	0.003	0.061	0.079
J _{FP}	0.008	0.008	0.008	0.008
Total calc.	1.276	1.071	0.971	0.809
Experiment ^b	1.33	1.05	1.06	0.85

^aThe intra PF₆⁻ group dipole-dipole contributions are zero as mentioned in the text.

^bTaken from Table II.

knowledge of the potential function constraining rotation of the PF_6^- group, and the calculations would be messy. On the other hand, if we assume that the PF_6^- ion jumps from one discrete orientation to another, identical one at a speed fast enough so that we can neglect the transit time, the second moment calculation is relatively simple. The intragroup dipole-dipole contributions to S_F are zero, inasmuch as they involve interactions averaged over the vertices of a regular polyhedron.³ Also, as shown in the Appendix, the average of each intergroup term of the form $(3\cos^2\theta-1)/r^3$ can be calculated in a straightforward manner.

The chief difficulty with this approach is that we are in fact dealing with two unknown structural features. In addition to the dynamic state of the PF_6^- group there is the question of the stable orientation of the group in the unit cell. S_F is sufficiently sensitive to the latter feature that by adjusting it we can fit the experimental S_F 's with the six-position dynamic model.¹⁷ But the differences between the experimental S_F 's and those calculated for the spherical rotation model are small, and the main evidence that the six-position model is more nearly correct comes from the reasonableness, on electrostatic grounds, of the PF_6^- group orientations required by it.

In Fig. 1 scale drawings are shown of the 100 planes of the four salts. The ionic radii of Pauling⁹ are used for the cations, while PF_6^- is assumed to be spherical with a diameter of 5.38 Å. The latter value was obtained by considering the cationic and unit cell dimensions summarized in Table 1. It is seen that the change in unit cell length is comparable to the change in the ionic diameter of the cation in going from one salt to the next in this series, with the exception of the change in going from the potassium salt to the sodium salt. In the latter case, a decrease of 0.76 Å in the diameter of the cation is accompanied by only a 0.10 Å decrease in the unit cell length. This implies that in the sodium salt the hexafluorophosphate ions are touching,

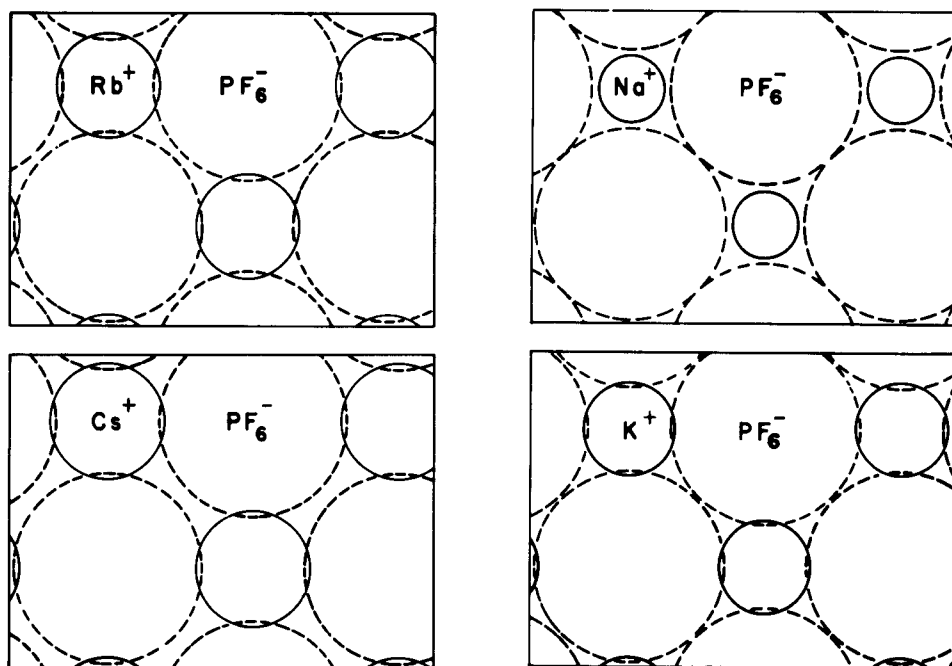


Fig. 1. The 100 planes of the four alkali fluorophosphates, for the NaCl-type, face centered cubic phase. An effective diameter of 5.38 Å is used for the PF_6^- group and Pauling's values for the cationic radii.

thus preventing a decrease in the unit cell length commensurate with the decrease in the ionic diameter of the cation. With this assumption, the "effective diameter" of the hexafluorophosphate ion is calculated from the unit cell length to be $(1/2)(2)^{1/2} \times 7.61 \text{ \AA} = 5.38 \text{ \AA}$. This value is supported by an estimate based upon the observed bond lengths. The P-F bond length is 1.58 \AA, and taking one-half the shortest F-F distance in the octahedral ion as the radius of the fluorine atom, one obtains $r_F = (1/2)(2)^{1/2} \times 1.58 \text{ \AA} = 1.117 \text{ \AA}$. These distances lead to a "diameter" for the PF_6^- ion of 5.39 \AA.

NaPF_6 .- On the basis of Fig. 1 it seems probable that in the sodium salt, the most favored orientation for the hexafluorophosphate ion is one in which the P-F bonds are aligned with the edges of the unit cell, that is, each P-F bond points toward one of the six sodium ions which octahedrally surround the PF_6^- . The ionic attraction between the negatively charged fluorine atoms and the sodium ions is probably greatest in this configuration and the repulsions between fluorine atoms in adjacent groups are small. The orientation of the ions in this structure is shown in Fig. 2 which includes two PF_6^- and two Na^+ ions. The method outlined in the Appendix was used to calculate the intergroup dipolar contributions to S_F from nearest neighbors. The contribution from the fluorine nuclei in the twelve nearest neighbor PF_6^- ions is 0.927 G^2 , compared with 0.939 G^2 for the spherical rotation model. Similarly, the broadening due to the six nearest Na^+ ions is 0.187 G^2 which is much larger than the 0.110 G^2 found for this contribution using the random reorientation model. This is due to the fact that in the six-position model, the P-F bonds are directed preferentially toward one of the six nearest neighbor sodium ions. The contributions of the sodium, phosphorus, and fluorine neighbors other than the nearest were calculated using the random reorientation model since their contributions are small and should not be a very sensitive function of the orientation of the PF_6^- octahedra.

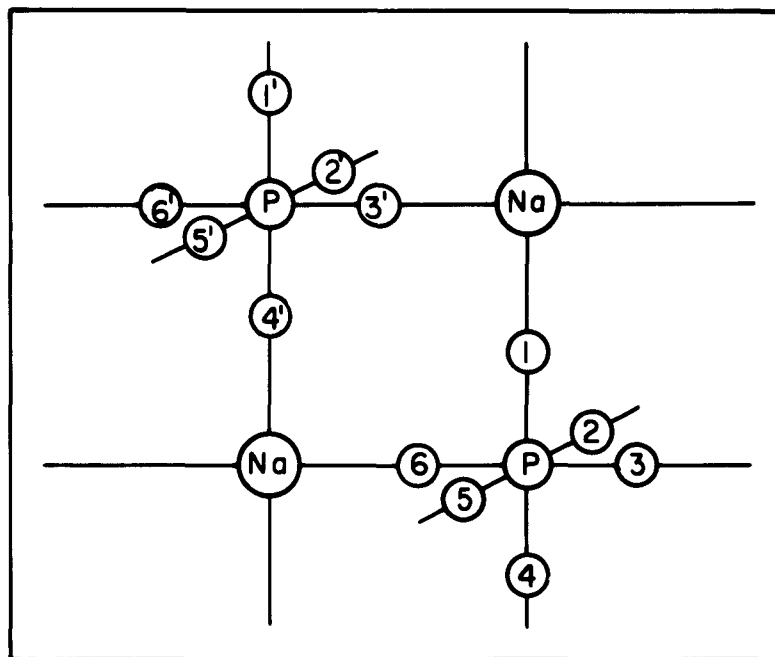


Fig. 2. The configurations postulated for the PF_6^- ions in NaPF_6 .

The results of these calculations are summarized in Table IV where they are compared with those for the spherical, random rotation model. The greatest difference, $\sim 0.08 \text{ G}^2$, is in the term for sodium nuclei, with the other changes very small and in the opposite direction. The calculated, total value for S_F is 1.276 G^2 for the spherical rotation model, and 1.340 G^2 for the six-position model. The agreement between the latter and the experimental values of $1.32 \pm 0.03 \text{ G}^2$ and $1.35 \pm 0.03 \text{ G}^2$ at 26°C and 98°C , respectively, is quite satisfying, though one cannot claim that this model is unique in predicting the value of the second moment, particularly when one allows for the errors in the experimental value.

K, Rb and CsPF₆.- For the other salts, the situation is not as clear cut. In the potassium salt, if a P-F bond points towards one of the neighboring potassium ions, the electron cloud of the fluorine atom overlaps that of the cation, as may be seen in Fig. 1. This makes unstable that orientation of the PF₆⁻ ion with each P-F bond pointing toward one of the six neighboring cations. On the other hand, the lattice has expanded very little from that of the sodium salt, so the repulsions between fluorine atoms on neighboring PF₆⁻ ions can still be appreciable. The probable result is that the P-F bonds are canted away from the edges of the unit cell. Some support is given to this hypothesis by the x-ray data of Bode and Clausen.⁵ Also, this structure in combination with the six-position model is as compatible with the value $1.05 \pm 0.03 \text{ G}^2$ observed for S_F as is the value of 1.07 G^2 calculated for the spherical rotation model.

For NaPF₆, the values of S_F calculated for the two models differ mainly in the F-Na contribution, as shown in Table IV. However, for KPF₆ this contribution is negligible for both models because of the non-magnetic nature of K⁴⁰. Moreover, the F-F contribution for a slightly canted PF₆⁻ orientation in the six-position model is virtually identical with that for the spherical rotation model, while the F-P and J_{FP} contributions are the same. So S_F for a

Table IV. Contributions in Gauss² to the F¹⁹ second moment in NaPF₆ calculated on the basis of the spherical, random rotation model compared with those calculated for the six-position model.

Model	F-F ^a	F-P ^a	F-Na	J _{FP}	Total
Spherical rotation	1.131	0.016	0.121	0.008	1.276
Six-position	1.119	0.015	0.198	0.008	1.340

^aThe intra PF₆⁻ group dipole-dipole contributions are zero as mentioned in the text.

slightly canted six-position model for KPF_6 is $\sim 1.07 \text{ G}^2$ and indistinguishable from S_F for spherical rotation.

In the rubidium and cesium salts, the lattice is appreciably expanded over the sodium and potassium salts. The overlap of the fluorine atom and the cation is greater than in the other salts when the P-F bond is directed along the cell edges, being about 0.25 Å. Thus qualitatively one would expect again that the fluorine atoms would not lie along the edges of the unit cell but rather would point more towards neighboring PF_6^- ions than they did in the potassium salt. Since the lattice has expanded, the minimum distance between fluorine atoms in adjacent PF_6^- ions is larger, and hence the repulsions between fluorine atoms in adjacent PF_6^- ions will be lower than in the potassium salt.

If the P-F bonds are directed more towards adjacent PF_6^- ions rather than the cations, one would expect the F-F contribution to the second moment to be larger for the six-position model than the value calculated for spherical reorientations. Calculations similar to those made for NaPF_6 indicate that the F-F broadening in a six-position model can be as much as 0.14 G^2 larger than that for spherical rotation, depending upon the relative orientations chosen for the PF_6^- groups. The F-P, F-Rb, and F-Cs contributions are small and do not decrease by more than about 25% on going from the spherical rotation to the six-position model, so S_F for the latter may be as much as 0.1 G^2 greater than for the former. Therefore, the fluorine second-moment data provide qualitative support of the six-position model for RbPF_6 and CsPF_6 , with the PF_6^- groups oriented such that the P-F bonds are canted off the edges of the unit cell.

Observations of phosphorus and of the alkali metal ions

In principle, further evidence as to the dynamic state of the PF_6^- ions could be obtained by observing the P^{31} nuclear resonance and that of the metal ion. However, for P^{31} the intragroup dipolar interactions are averaged out by either the spherical or six-position type reorientations, and the intergroup distances are larger than those for F^{19} so that the two models for the dynamic state of the PF_6^- group give virtually identical values of S_p ($\sim 0.9 \text{ G}^2$ for NaPF_6).¹⁸ On the other hand, the resonance from the metal ion is quite sensitive to the nature of the PF_6^- group motions.

However, all the alkali metal nuclei present in detectable quantities have quadrupole moments, and unless the nucleus is in a position where the electric field gradient is zero, the lines will be broadened by the interaction of the quadrupole moment with the electric field gradient. A field gradient approaching zero seems possible in the case of the sodium salt, but it seems somewhat less likely in the other salts. The Na^{23} nuclear magnetic resonance was observed in NaPF_6 at lower temperatures, -60° to -70°C , to improve sensitivity. Nonetheless, the signal to noise ratio was poor and the spread in S_{Na} values was very large. The average second moment from six spectra is 2.6 G^2 , but the values range from 1.8 to 3.7 G^2 . The values calculated for the spherical rotation and the six-position models, assuming the room temperature crystal structure, are 1.97 G^2 and 3.13 G^2 , respectively. Unfortunately, in spite of their large difference, both of these values lie within the range of values found. Moreover, it is not certain that the NaPF_6 structure is the same at -60° to -70°C as at room temperature, although the temperature dependence of S_p reported in the next section shows no change in this range.

B. Temperature Dependence of the PF_6^- Reorientations

In Fig. 3 there is plotted the temperature dependence of S_F observed for finely powdered samples of the four hexafluorophosphates over the region studied. Some of the points represent averages of second moments at closely spaced temperatures; such averaging simplified the plotting and makes the general trends more readily discernible. For the sodium and potassium salts the F^{19} second moment increases by a factor of ten upon cooling below room temperature, with the change for KPF_6 centered 20° below that at 155°K for NaPF_6 . The change in S_F for RbPF_6 is not complete at the lowest temperature at which measurements were made, but it appears to be centered at about 90°K . For the cesium salt, on the other hand, S_F increases very little, only 0.1 G^2 , even at 65°K (obtained by pumping on the liquid nitrogen used in the cryostat). At first it may seem surprising that such a large ion would still be reorienting at such low temperatures, but it must be remembered that the hexafluorophosphate ion is highly symmetric and that these anions are kept from close contact with each other by the large cesium ions.

In any event, the qualitative trend is clear for the four salts. The ease and rate at which the PF_6^- groups reorient increase with increasing size of the alkali metal cation. And this seems reasonable inasmuch as the potential barriers must arise in large part from electrostatic interactions between the PF_6^- and M^+ ions, and these would be smaller for the larger cations.

Low temperature state of NaPF_6 and KPF_6

In the sodium salt, the F^{19} second moment has reached an apparent limiting value of about 15 G^2 at liquid nitrogen temperatures. The resonance line tends to saturate very easily when the line has broadened to near its maximum value, and this combined with the low signal to noise ratio encountered resulted in considerable scatter of the experimental points at low temperatures.

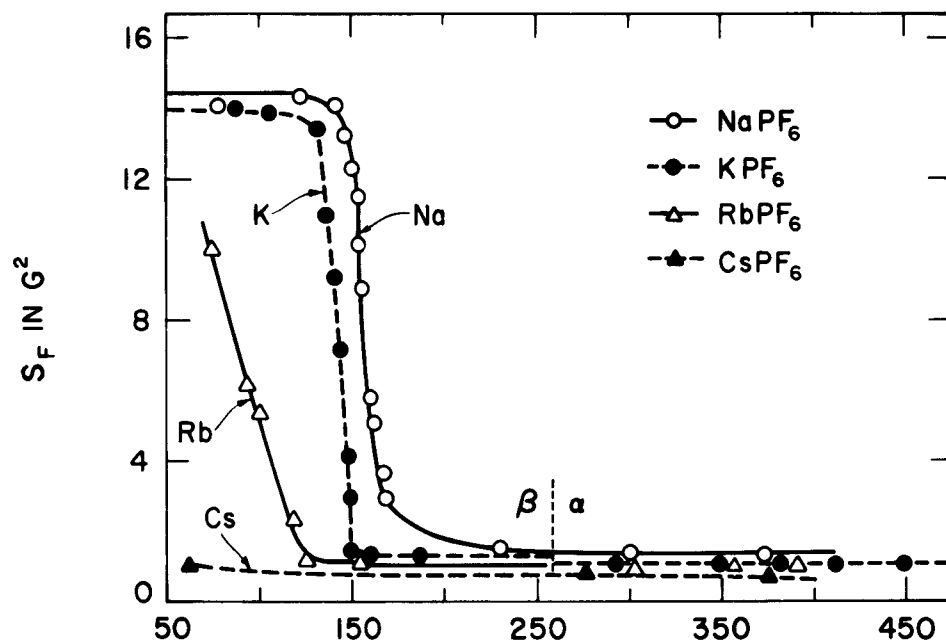


Fig. 3. The F^{19} second moment versus temperature, as observed for finely powdered samples of the alkali metal fluorophosphates. The dashed vertical line at $\sim 260^\circ K$ indicates a phase transition for KPF_6 .

If we assume that the crystal structure is the same below the region where the second moment is changing as it is at room temperature and that the P-F bonds point along the unit cell edges, the rigid lattice second moment is calculated to be about 15.5 G^2 . This value for S_F includes intragroup F-F and P-F contributions of 10.5 and 1.7 G^2 , respectively, an F-F contribution of 2.5 G^2 from the 12 nearest neighbor PF_6^- ions, 0.5 G^2 from the six nearest neighbor Na^+ ions, and 0.3 G^2 the remaining several small terms.

The crystal structure of NaPF_6 is not known at low temperatures, but it is difficult to conceive of a structure in which the intergroup contribution to S_F could vary from the calculated value by more than $\pm 50\%$. Even then the intragroup contributions to S_F for reorientation about a two-, three-, or four-fold axis are much too small to account for the 15 G^2 value observed at low temperatures, so we conclude that the "rigid lattice" has been obtained at temperatures below the change in second moment. At these temperatures, the resonance line is about 50,000 cps wide (between points of maximum slope), and the rate of PF_6^- ion reorientation in the rigid lattice must be appreciably less than 50,000 times per second.

In the potassium salt, S_F reaches a value of 14 G^2 at low temperatures. This is slightly smaller than that found in the sodium salt. Nonetheless, it is in good agreement with the rigid lattice model. This is due in part to the K-F term being negligible while the corresponding Na-F term in NaPF_6 is 0.5 G^2 . Furthermore, all of the intergroup terms in KPF_6 are reduced somewhat from those in NaPF_6 because of the difference in unit cell size. There appears to be a small change in S_F for KPF_6 at about -15°C ; this is no doubt associated with the phase change to a trigonally distorted b.c.c. unit cell ($a = 4.85 \text{ \AA}$, $\alpha = 94^\circ$), at lower temperatures.¹⁹

Activation energy for PF_6^- reorientations

The dependence of the second moment upon temperature can give information about the height of the barrier to reorientation and about the frequency factor for this process, and one would hope to be able to obtain this information from the temperature dependence studies of S_F . Several similar equations have been derived^{1,11} which relate the second moment (or the linewidth) to the barrier height and to the frequency factor. The one employed here is the following one, used by Waugh,¹ and his coworkers,

$$S = S_{HT} - (S_{LT} - S_{HT})(2/\pi) \tan^{-1}[\alpha \tau_0 S^{1/2} \exp(\Delta E/RT)] \quad , \quad (5)$$

where the subscripts HT and LT refer to the high and low temperature limits of the second moment S observed at temperature T , α is a line-shape parameter of order unity, ΔE is the barrier height, and τ_0 an inverse frequency factor. Upon rearranging this equation and taking logarithms, one obtains

$$\log P \equiv \log[S^{-1/2} \tan(\pi/2)(S - S_{HT})/(S_{LT} - S_{HT})] = \log(\alpha \tau_0) + \Delta E/2.303RT \quad . \quad (6)$$

A plot of $\log P$ versus $1/T$ should give a straight line of slope $\Delta E/2.303R$.

Such a plot is given in Fig. 4 for NaPF_6 . Fitting the data visually with a straight line yields a value for ΔE of 5.5 kcal/mole with an uncertainty of 1 kcal. However, the actual error probably is larger. In Eqs. (5) and (6), α is an undetermined constant which depends upon the lineshape. If a particular lineshape is maintained while the width changes, α remains constant and appears only in the intercept of the plot of $\log P$ versus $1/T$. But if the lineshape changes with temperature, α will change as will the apparent slope of the $\log P$ versus $1/T$ plot. A convenient measure of the line shape is the ratio of the linewidth to the square root of the second moment. This ratio is 3.1 at temperatures just above and below the line width change, but it is only

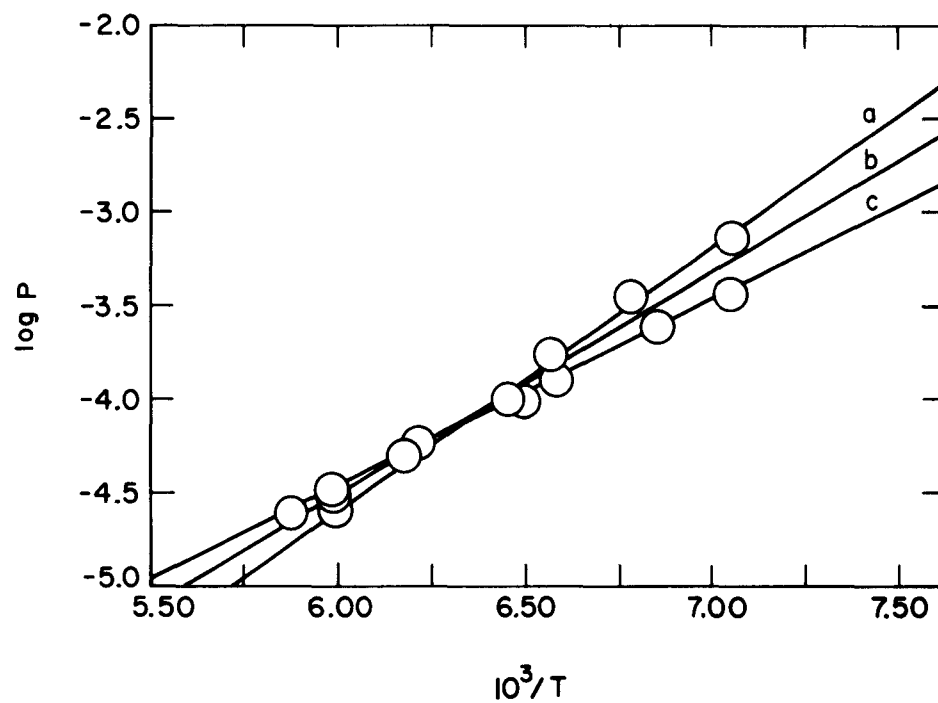


Fig. 4. A plot of $\log P$, as defined in Eq. (6), versus $10^3/T$ for S_F in NaPF_6 . The slope of the best-fit line b corresponds to a potential barrier ΔE of 5.5 kcal/mole to the PF_6^- group reorientations. Lines a and c give uncertainty limits to ΔE of ± 1 kcal/mole.

1.5 at 155°K, the center of the change. The actual changes in line shape in this region are shown in Fig. (5). It is clear that the tails of the line broaden considerably before the linewidth changes appreciably. Thus α is not a constant, which leads to uncertainty in the value of the height of the barrier to reorientation.

The failure of α to remain constant indicates that the model used in the derivation of Eq. (5) does not apply quantitatively to the case of NaPF_6 . Equation (5) is expected to apply in cases where the resonance is broadened by the freezing out of motion(s) described with a single correlation time τ_c . However, each possible mode of reorientation of the PF_6^- ion, described in Section III.A, may have a different potential barrier and frequency factor and, therefore, a different correlation time with a different temperature dependence. If the line-width changes associated with different types of motion occur too close in temperature to be resolved, the line-width and line-shape changes are complex functions of temperature, as observed. However, the arc-tangent curve is not sensitive to such complexities, and the straight-line plot found in Fig. 4 for the second-moment data provides an average sort of ΔE rather than a proof that Eqs. (5) and (6) apply rigorously. Furthermore, as discussed in the section following, the line-width and line-shape changes, at least for KPF_6 and RbPF_6 , are very sensitive to the physical state and thermal history of the sample and this discouraged us from further attempts to evaluate the ΔE 's involved.

C. Thermal Hysteresis and Particle Size Effects

The results presented in the preceding section were obtained on samples in the form of very fine powders. These results are reproducible and exhibit no apparent thermal hysteresis. However, it was found that the temperature dependence of the fluorine resonance in larger crystallites of KPF_6 and RbPF_6

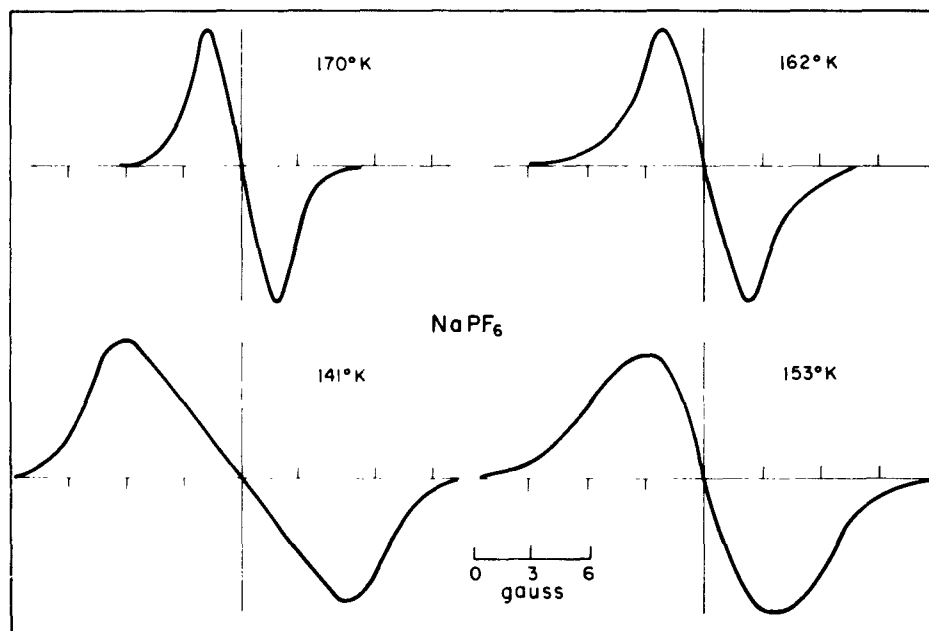


Fig. 5. First derivatives of the F^{19} NMR absorption observed in $NaPF_6$ at several temperatures in the region of changing line shape and second moment. The centers of the lines correspond to a magnetic field of about 6300 G.

depends markedly upon particle size and previous physical treatment of the sample. The results in Fig. 3 imply that the apparent absence of such effects for CsPF_6 is due to our experiments not extending to low enough temperatures to affect the line width for any "physical state" of the solid. In the case of NaPF_6 , the special recipe required to prepare the sample leads only to a very fine powder. The anhydrous sodium salt can not be prepared from a saturated aqueous solution as can the other salts;²⁰ the monohydrate precipitates instead. The anhydrous NaPF_6 is prepared by dessication of the monohydrate with sulfuric acid or other powerful drying agent and the resulting sample is a very fine powder.

Rubidium Hexafluorophosphate

Dependence of S_F and line shapes upon physical treatment of sample.-

For RbPF_6 we were able to obtain the most extensive data, so the results for it will be given first. Polycrystalline samples, in the form obtained upon crystallization from aqueous solution, when cooled for the first time give F^{19} spectra which differ very markedly from those summarized in Fig. 3 for a finely powdered sample. Instead of the simple line shapes found for the latter, which are very similar to those given in Fig. 5 for NaPF_6 , one finds a broad component increasing in intensity and a narrow component decreasing in intensity as the temperature is lowered. Line shapes typical of this behavior are shown in Fig. 6. Furthermore, although the RbPF_6 is nicely crystalline before cooling, it appears to be a fine powder after being cooled to liquid nitrogen temperatures and allowed to return slowly to room temperature, which was usually done in a period of about ten hours. Moreover, when the sample is cooled a second time, there is only a very faint hint of a broad component at the lowest temperatures studied and the line appears to broaden more or less continuously in the same manner as in the sodium salt. It is not possible to distinguish the broad and narrow components seen so clearly upon cooling the first time.

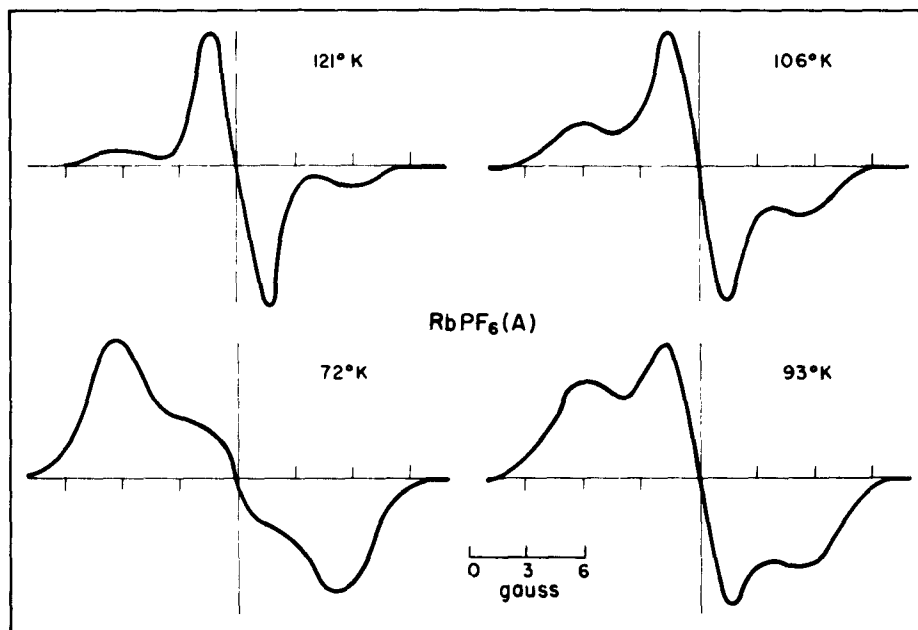


Fig. 6. First derivatives of the F^{19} NMR absorption observed at several temperatures upon the first cooling cycle for a sample of $RbPF_6$ (A) obtained upon crystallization from a saturated aqueous solution. The centers of the lines correspond to a magnetic field of about 6300 G.

Because of the complex shape, the linewidth is not a good measure of the broadening in the sample being cooled the first time, so the second moments were determined for both types of behavior. Figure 7 shows the results for samples being cooled the first time, RbPF_6 (A), and for samples being cooled the second time, RbPF_6 (B). There are also the second moment data given in Fig. 3 for a "fresh" sample, RbPF_6 (C), which was ground with a mortar and pestle for several minutes, during which it quickly acquired the consistency of face powder. These results are plotted also in Fig. 7 and it is seen that the S_F 's agree within experimental error (as do the line shapes) with those for an ordinary sample being cooled for the second time.

For both the thermally and mechanically powdered samples the onset of broadening upon cooling occurs at a much lower temperature ($\sim 25^\circ$) than in fresh samples (A) being cooled the first time, and at any given temperature in the region of changing linewidth, the second moment is less. High accuracy is not claimed for the second moment values for two reasons. First, the broad component in RbPF_6 (A) saturates very easily, and secondly, it appears that there is a small chemical shift between the center of the broad component and the center of the narrow component.²¹ Both factors lead to uncertainties in the apparent second moments. The purpose of presenting these data is to show that the line broadening does set in at different temperatures in the two cases and that the possibility of the second moment being the same at a particular temperature, even though the lineshape is not the same, is ruled out.

One of the components of the line of RbPF_6 (A) is about three gauss wide which is the width of the line at room temperature and corresponds to nearly random reorientation. This component decreases in intensity as the temperature of the sample is lowered. The second component is about twelve gauss wide which is the width of the fluorine resonance observed in the sodium salt below the temperatures where the line broadens. This component increases in

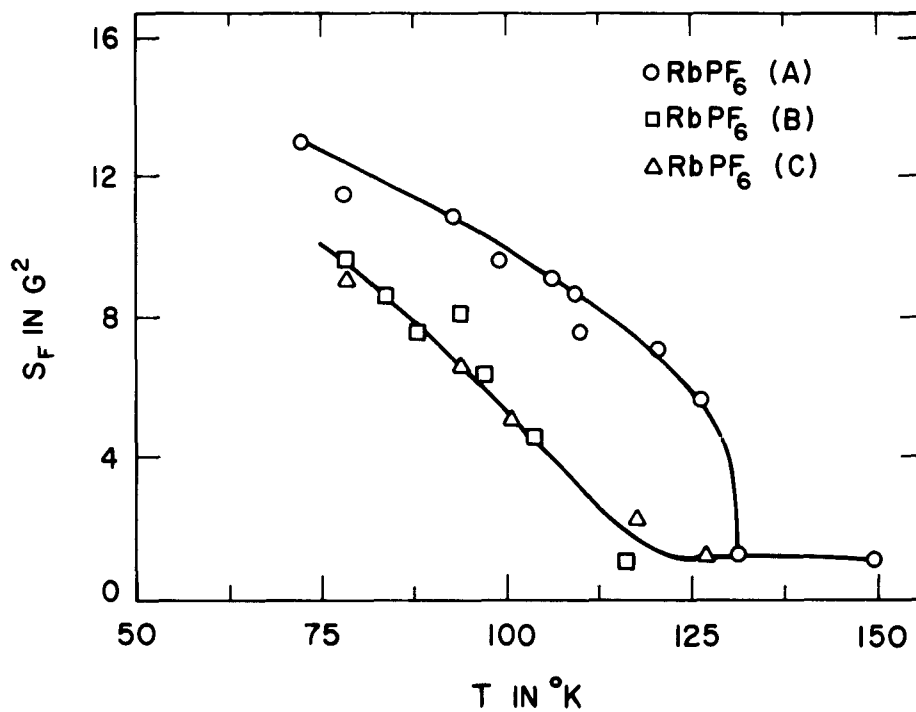


Fig. 7. The ^{19}F second moment versus temperature, as observed for RbPF_6 under several conditions: (A) A polycrystalline sample upon its first cooling cycle, (B) Sample A upon its second cooling cycle, and (C) A "fresh" sample ground mechanically into a fine powder before cooling.

relative intensity as the temperature is lowered. One is forced to conclude that at every temperature studied below 130°K there are two types of PF_6^- ions present: those reorienting at a rate greater than the frequency width of the line, and those reorienting at a rate slower than the frequency width of the line. The former give the narrow component and the latter, the broad. When the temperature is lowered, the fraction of the groups which are reorienting fast enough to narrow the line decreases, as does the intensity of the narrow component. One cannot say whether there are some PF_6^- ions which are reorienting at a frequency comparable^{to} the line width or some reorienting about restricted axes; both types would give rise to a line of intermediate breadth. However, the fraction of PF_6^- ions in either of these situations is small, otherwise one could not distinguish the narrow and broad components.

This very peculiar behavior must be contrasted with the results obtained for the two types of powdered samples. In them, the line broadens more or less continuously, which is the behavior normally encountered in molecular crystals with rotator phases. Furthermore, why do relatively large crystallites crumble into a fine powder during their first cycle to low temperatures? To account for these effects, the following model is proposed.

A model for the effects observed.- The RbPF_6 is present originally in the form of relatively perfect crystallites, that is, it crystallizes with few imperfections. Upon cooling to 130°K, some PF_6^- ions stop reorienting and occupy a position in the unit cell such that they prevent some or all of the PF_6^- ions in neighboring unit cells from reorienting. This cooperative process is bounded by imperfections which prevent transmission of the "locking effect". A phase change is almost certainly associated with the transition to a rigid lattice. In different regions of the crystals, this effect will occur at different temperatures, depending upon the nature and number of imperfections and impurities present. Thus at any one temperature there will be two types of PF_6^- ions, those in a rigid lattice and those which are

reorienting. At 77°K, almost all ions are in rigid lattice sites. Upon warming the salt, it again passes through the phase change to liberate the frozen PF_6^- ions, and imperfections are introduced into the crystallites during this phase change. It may be possible for defects to be introduced in the "unlocking" of the PF_6^- ions without a phase change occurring, but this appears quite unlikely. Upon a subsequent low temperature cycle, the imperfections prevent the cooperative locking process from extending over more than a few neighbors. Moreover, there would be a distribution of sites for PF_6^- ions depending upon the distribution of imperfections and their nearness to the PF_6^- ions. The corresponding distribution in the barriers hindering the PF_6^- reorientations and the superposition of spectra from all the types of PF_6^- ions present could then give rise to a line which would broaden as the temperature was lowered and one in which the individual components could not be distinguished.

This model, as it must, does predict the correct line shape found for the original crystallites upon cooling the first time and a line shape compatible with that observed upon cooling for the second time. At the same time it predicts that a relatively large number of crystalline imperfections are produced upon warming the sample from liquid nitrogen temperatures. It is presumably these imperfections which are associated with the crumbling of the crystalline sample that is observed upon return to room temperature. The onset of broadening upon cooling the second time occurs at a lower temperature than upon cooling the first time, indicating that the barrier to reorientation (or the average barrier to reorientation) is lower when the imperfections are present. This indicates that the imperfections are of the vacancy or dislocation type, since these would most likely lower the barrier to reorientation for nearby PF_6^- ions. This is consistent with the model proposed, in that the ionic attractive forces in the crystal are not extremely strong due to the large diameters of the univalent ions present.

The chief objection, perhaps, to the model is the relatively large number of imperfections which must be introduced into the solid to change the behavior of the sample so drastically. However, the fact that mechanical grinding produces the same effects as does the thermal cycling leaves little doubt as to the qualitative correctness of the model proposed. The lack of crystal structure data for RbPF_6 at low temperatures prevents one from proposing a detailed mechanism for the "locking effect" and remaining on solid ground at the same time. Going out on a limb, however, one can reason in the following manner.

The rubidium salt is very similar to the potassium salt, in that the room temperature crystal structure of each is too compact to permit the P-F bonds to point along the unit cell edges toward the nearest cations. At about -15°C , the potassium salt undergoes a phase change to a low temperature structure based on a trigonally distorted body-centered cubic unit cell ($a = 4.85 \text{ \AA}$, $\alpha = 94^\circ$). Since in addition, the F^{19} spectrum of KPF_6 exhibits some of the peculiar features of the rubidium salt at temperatures on the order of 170°K , it is likely that the rubidium salt also undergoes a transition to a body-centered form at low temperatures. Assuming that such a transformation does occur above 135°K in the rubidium salt, a reasonable estimate of the cell length a for this crystal structure would be 5.0 to 5.1 $\text{\AA}$. The "diameter" of the PF_6^- ion along a F-P-F axis is at least 5.4 $\text{\AA}$, so it is evident that any reorientation which occurs must be cooperative with the neighboring PF_6^- ions. The protrusion of part of the fluorine atom into the neighboring unit cell couples the motion of the neighboring PF_6^- ions. If, either through the action of an impurity or a crystalline imperfection, or because of loss of energy upon cooling, one PF_6^- ion stops reorienting and remains in a position such that some or all of the P-F bonds are directed toward the faces of the (distorted) cube, then the neighboring PF_6^- ions are effectively prevented from reorienting and the cooperative effect postulated can occur.

Lustig² found in his study of RbPF_6 that the fluorine resonance did not broaden noticeably upon cooling to 77°K. The reason for the difference in the results obtained is almost certainly that his samples of the rubidium salt contained larger concentrations of imperfections and impurities than did the samples used in our study.

Potassium Hexafluorophosphate

The behavior of KPF_6 is similar in part to that just discussed for RbPF_6 . The F^{19} line shapes for a mechanically powdered sample change gradually with temperature. They are like those for NaPF_6 in Fig. 5, except that as for RbPF_6 there is a hint of distinguishable broad and narrow components at the low temperature end of the line-width changes (140°K for KPF_6 and 80°K for RbPF_6). Also, the absorption of recrystallized and unground samples, A, B, and C, broadens at higher temperatures and has different widths (and shapes) from that of powdered samples, D, as shown by the temperature dependence of S_F in Fig. 8.

However, as given in Fig. 8, there is considerable difference between the behavior of two of the recrystallized samples (A) and the other recrystallized samples (B) as well as the original unground sample (C), with B and C behaving the same. Both of the A samples were first samples from a recently crystallized batch of KPF_6 and tended to contain the larger polycrystalline material. Only these two samples exhibited clearly distinguishable broad and narrow components in the line shape; typical examples are given in Fig. 9 and comparison with Fig. 6 reveals their similarity to unpowdered RbPF_6 upon its initial cooling. But the spectra of this KPF_6 (A) were unaffected by the thermal cycle. In these spectra, the signal-to-noise was poor because of saturation effects so the data are less accurate. With this qualification, the line shapes and S_F for KPF_6 (A) were the same upon the second cooling cycle as the first.

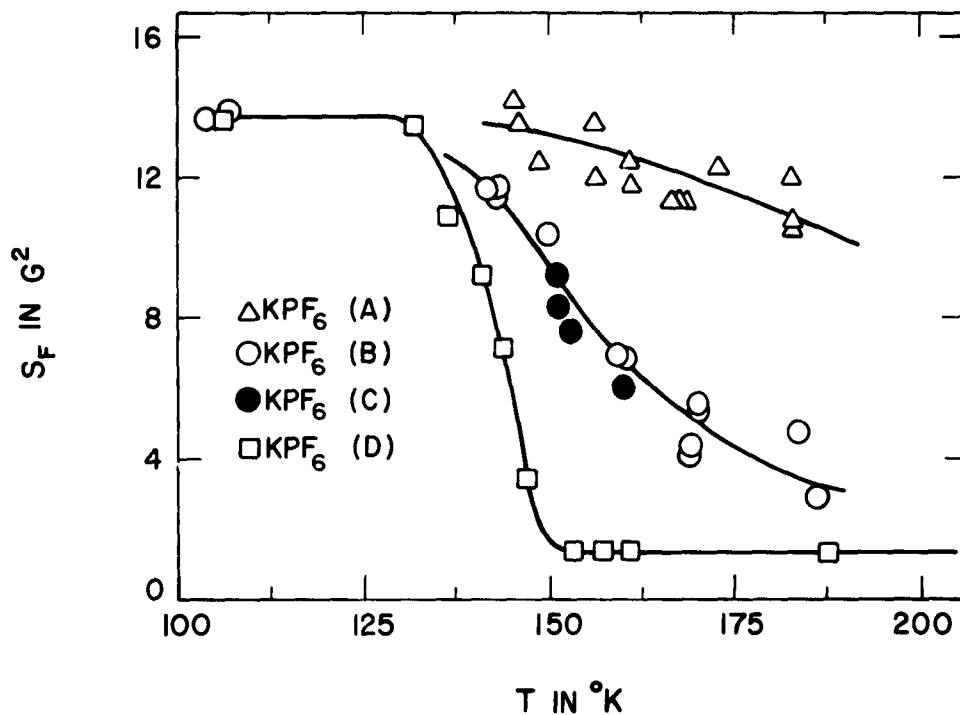


Fig. 8. The F^{19} second moment versus temperature, as observed for KPF_6 under several conditions: (A) Two recrystallized samples upon first and second cooling cycles, (B) Other recrystallized samples, (C) The original unground sample, and (D) The original sample ground into a fine powder.

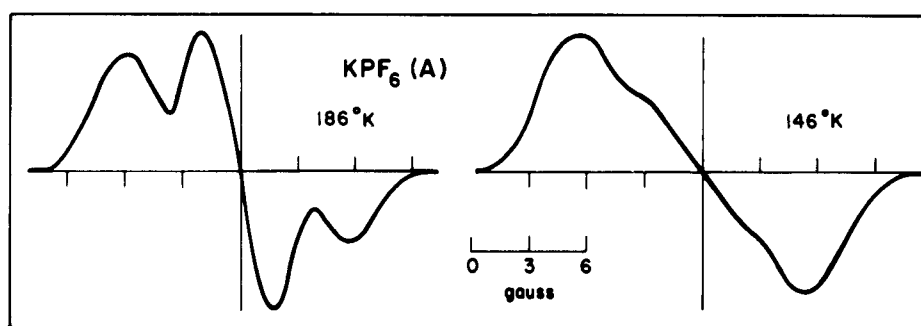


Fig. 9. First derivatives of the F^{19} NMR absorption observed at temperatures in the range of changing line width for a selected sample (A) of recrystallized KPF_6 .

Moreover, thermal effects were not noted for the other unpowdered samples, B and C, nor did the physical state of any sample appear to change during a thermal cycle.

These results can be interpreted in terms of the same general model proposed for KbPF_6 , modified to account for the differences in behavior. The absence of thermal cycling effects in KPF_6 could be because it does not undergo a phase transformation, or undergoes a much milder one, once the reorientation of the PF_6^- ions ceases and that, therefore, defects are not produced in great numbers upon warming to room temperature. Another possibility is that in the potassium salt, due to the greater charge density on the smaller cation, the ionic bonding is strong enough to prevent the formation of large numbers of defects upon passing through a phase change. The differences in behavior for the various unpowdered samples could result from a greater sensitivity of the dynamic structure to impurity and/or imperfection concentrations and of their dependence on the crystallization conditions.

Again, the results obtained by Lustig² are somewhat different. He observed an onset of broadening at about 175°K and a limiting second moment at low temperatures of about 19 G^2 . His limiting value at low temperatures is about 5 G^2 larger than that observed in this work. It must be admitted, however, that when the resonance has broadened to near its rigid lattice value, saturation effects were a problem in our measurements of S_F . On the other hand, Lustig's value for the second moment at high temperatures, 0.9 G^2 at 293°K, is somewhat lower than that observed in our work. Lustig also obtained a value of 2 kcal/mole for the barrier to PF_6^- reorientation. However, the complexity of our results, including the presence of two components in the absorption from groups in different motional states, have discouraged us from making such an analysis.

D. Reinterpretation of Previous Results for CF_4

Recently, Aston, Stottlemeyer, and Murray²² observed broad fluorine resonance lines growing at the expense of narrow lines upon cooling carbon tetrafluoride. In that the behavior they observed is outwardly similar to that observed upon cooling RbPF_6 for the first time, it is appropriate to compare their results with ours.

They found a broad line (II) increasing in intensity at about 76°K as the narrow line (I) decreased in intensity. Upon cooling to 73° K the narrow line disappeared. The narrow line (I) was ascribed to CF_4 molecules which are reorienting and diffusing simultaneously, and line (II), which has $S_F \approx 2 \text{ G}^2$, was ascribed to molecules which are reorienting but not diffusing. Upon cooling the sample to 65°K, they found a still broader line (III). As the temperature was lowered further, the intensity of line III increased as that of line II decreased, until at 55°K line II could no longer be detected. The authors suggested that the lattice is rigid below 55°K, and that upon warming, rotation about a C_2 axis is the first motion to narrow the resonance, giving line II. That the lattice is rigid below 55°K is reasonable.

However, one can show by the methods used in Section III.A that random reorientations of the CF_4 molecules would give a value for S_F of at least 1.7 to 1.9 G^2 , which is a result of the intermolecular interactions alone and which is quite close to the 2 G^2 observed for line II. This calculation was performed by assuming a simple cubic or body-centered cubic structure with the unit cell dimension determined by the density²³ of carbon tetrafluoride, 1.96 g/ml at 89°K, the melting point. Moreover, C_2 reorientation would give an S_F appreciably larger than the 2 G^2 observed. The intermolecular contribution would be between that calculated for random reorientation and that for the rigid lattice ($\sim 3.5 \text{ G}^2$). A reasonable estimate is 2.5 G^2 , which combines with the 1.2 G^2 calculated for the intramolecular contribution to give a

predicted total value of 3.7 G^2 . Therefore, we suggest that line II corresponds to random or nearly random reorientation of the CF_4 molecules. All of the molecules are in this state at temperatures between 65°K and close to the λ -point at 76°K . Above the λ -point, the CF_4 molecules are not only reorienting but also diffusing, giving the narrow line observed in the solid just below its melting point.

In the temperature interval between 55° and 65°K the two broad lines correspond to CF_4 molecules in rigid lattice domains (line III) and molecules in domains where the random or near random molecular reorientations average out the intramolecular dipolar broadening to give the other broad line (II). This two phase behavior is consistent with a cooperative locking together of the CF_4 molecules, inhibited by vacancies whose concentration decreases at lower temperatures. The similarity of the CF_4 results to those we obtained for RbPF_6 and KPF_6 leads us to suggest that this type of behavior may be relatively common for groups of high symmetry, with moments of inertia such that quantum mechanical tunneling is unimportant.

ACKNOWLEDGMENT

We wish to thank Dr. Wayne E. White of the Ozark-Mahoning Co. for the samples and their analyses, and Dr. Clive Coogan for many interesting discussions of reorientations of ions in solids.

APPENDIX

In the calculation of effective second moments for particular types of restricted motion, the treatment of the intergroup contributions often is a chore. And this was found to be so in treating the six-position model for the PF_6^- reorientations. It does not seem essential to present the algebraic details,¹⁸ but an outline of the procedure may have some general interest. We are interested in evaluating terms of the form

$$\langle \langle (3\cos^2\theta_{1j}-1)/r_{1j}^3 \rangle_C \rangle_P, \quad (\text{A1})$$

where $\langle \rangle_C$ denotes the average of the function over the configurations occupied by the two nuclei considered and $\langle \rangle_P$ denotes the averaging for a crystal powder sample.

A fluorine in a given PF_6^- group has 36 "nearest neighbor" fluorines in the adjacent 6 PF_6^- groups. The positions and relative orientations of these groups are taken to be as shown in Fig. 2. The coordinate system used is that given in Fig. 10, with $\vec{H}$ the direction of the magnetic field and $\vec{r}$ a vector between two fluorine nuclei. Using these definitions, and the addition theorem of Legendre polynomials,²⁴ one obtains the following expression for $(3\cos^2\theta_{1j}-1)/r_{1j}^3$:

$$\begin{aligned} [2P_2(\cos\theta_{1j})/r_{1j}^3] &= (3\cos^2\theta_{1j}-1)/r_{1j}^3 \\ &= (2/r_{1j}^3) \left\{ P_2(\cos(\theta_1)_{1j}) \times P_2(\cos\theta_2) \right. \\ &\quad + 2 \sum_{m=1}^{\ell} \frac{(\ell-m)!}{(\ell+m)!} \times P_2^m(\cos(\theta_1)_{1j}) \\ &\quad \left. \times P_2^m(\cos\theta_2) \times \cos m[(\phi_1)_{1j}-\phi_2] \right\}. \end{aligned} \quad (\text{A2})$$

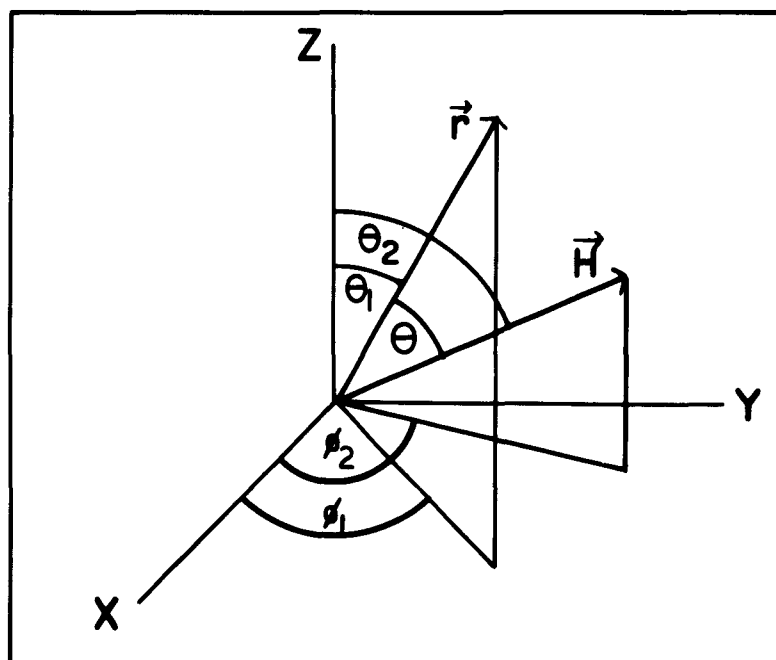


Fig. 10. Definition of the angles relating the internuclear vector $\vec{r}$ and the applied field direction $\vec{H}$.

The six neighboring PF_6^- groups are equivalent as are the six sites which a given fluorine may occupy. So we need to average Eq. (A2) over the 36 possible relative configurations of two fluorine atoms, square the resulting expression, and then average over θ_2 and ϕ_2 , that is, perform the powder average. The result of these calculations is the replacement of r_{ij}^{-6} in Eq. (2) with the following expression:

$$\begin{aligned} & \left[(1/36) \sum_{i=1}^6 \sum_{j=1}^6 \left[\frac{1}{2} (3 \cos^2(\theta_1)_{ij} - 1) / r_{ij}^3 \right] \right]^2 \\ & + (1/12) \left[(1/36) \sum_{i=1}^6 \sum_{j=1}^6 \left[3 \sin^2(\theta_1)_{ij} \cos 2(\phi_1)_{ij} / r_{ij}^3 \right] \right]^2. \end{aligned} \quad (\text{A3})$$

*Taken in the main from the thesis of G. R. Miller submitted to the Graduate College of the University of Illinois, in partial fulfillment of the requirement for the degree of Doctor of Philosophy in chemistry, 1962. This investigation was supported in part by the Office of Naval Research.

¹National Science Foundation Predoctoral Fellow, 1958-61. Now at the Physical Chemistry Laboratory, Oxford University, Oxford, England.

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- ¹⁷The P-F bond length is another parameter which affects S_F for this model, but not for the spherical rotation model. However, this is a secondary factor because the uncertainty in the 1.58 Å value which we use is probably no more than ± 0.02 Å. For both models, there might be a contribution to S_F from the anisotropy in J_{FP} and in the fluorine chemical shift; however, both of these are small to begin with and they would be further reduced by the PF_6^- group reorientations.
- ¹⁸Some experimental as well as the calculated values are given by G. R. Miller, Ph.D. Thesis, University of Illinois (1961).
- ¹⁹C. Finbak and O. Hassel, Z. physik. Chem. B32, 437 (1936).
- ²⁰This results probably from the great disparity in the sizes of the Na^+ and PF_6^- ions, while the even greater disparity in size between Li^+ and PF_6^- may be the reason why the lithium salt has not yet been prepared.
- ²¹The anisotropy of the fluorine chemical shift is the probable cause of this displacement. It would be averaged out for the narrow component but it would produce asymmetry and a shift of the broad component. See, for example, H. S. Gutowsky and D. E. Woessner, Phys. Rev. 104, 843 (1956).
- ²²J. G. Aston, Q. R. Stottlemeyer, and G. R. Murray, J. Am. Chem. Soc. 82, 1281 (1960).

²³Handbook of Chemistry and Physics (Chemical Rubber Publishing Co., Cleveland, Ohio, 35th ed., 1953), p. 838.

²⁴H. Margenau and G. M. Murphy, The Mathematics of Physics and Chemistry (D. Van Nostrand Company, Inc., New York, 2nd ed., 1956), p. 112.

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