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The ^{19}F Solid-State High-Resolution Nuclear Magnetic Resonance Study of K_2SiF_6, K_2GeF_6, and K_2SnF_6

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High-resolution ^{19}F NMR experiments were carried out on K_2SiF_6, K_2GeF_6, and K_2SnF_6, and the chemical-shift shielding tensors were determined. In all three substances, the shielding tensors are axially symmetric, and the most shielded direction is parallel to the MF (M=Si, Ge, and Sn) bond. The values of the shielding tensor elements ($\sigma_{//}$ and $\sigma_{\perp}$) change systematically from K_2SiF_6 to K_2SnF_6, except for the $\sigma_{\perp}$ component of K_2SiF_6, which is very large compared with those in the Ge and Sn-complexes. The analysis of σ's by a simple MO treatment indicates that π-backbonding is the strongest in the Si-F bond, probably because of the extraordinarily low electronegativity of Si. At room temperature, the reorientation of MF_6^{2-} anions is rapid enough to average out the shielding tensor components in the Si and Sn-complexes.

High-resolution NMR spectroscopy is a very useful technique for examining the structures and the chemical reactivities of such inorganic complex ions as MF_6^{2-} and is widely used for those ions in solutions. However, usual high-resolution NMR in solution gives only an averaged value of the chemical shift. In order to study the electronic structure and the reactivity of complex ions more closely, it is desirable to measure the anisotropy in the chemical-shift tensor by using crystalline materials. The temperature dependence of the chemical shift also provides valuable information about the very slow anisotropic molecular motion in the crystalline state.

It has been recognized that various types of compounds of Group IV_b metals, i.e., Si, Ge, and Sn, show unusual properties in that they do not obey the so-called law of corresponding states: the halogen nuclear quadrupole resonance frequencies in MX_4 (M=Si, Ge, and Sn) do not vary in a regular manner.[1] Also the ^{19}F chemical shift in MF_6^{2-} in solution does not change systematically from Si to Sn, etc.[2] These and other unique aspects of the behavior of the Group IV_b compounds have not yet been fully understood, although it can be inferred that the nature of the chemical bond changes abruptly on going from Si to Ge.[3] It is, therefore, interesting to determine the chemical shielding tensor completely using crystalline materials of Group IV_b compounds. Here we applied the solid-state high-resolution NMR technique to a series of K_2MF_6, where M=Si, Ge, and Sn, in an attempt to obtain detailed information on the electronic structure of MF_6^{2-} anions.

At room temperature, K_2SiF_6 is cubic,[4] while the other substances are trigonal,[5] as is shown in Figs. 1 and 2. The site symmetry at Si in K_2SiF_6 is O_h, while that of the central atoms in the other compounds is D_{3d}, which reflects the slight distortion of the MF_6 polyhedra from the regular octahedron. All the

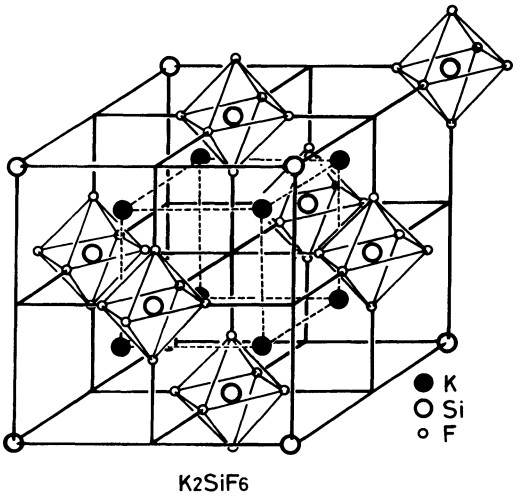

Fig. 1. Structure of K_2SiF_6. After Ref. 4.

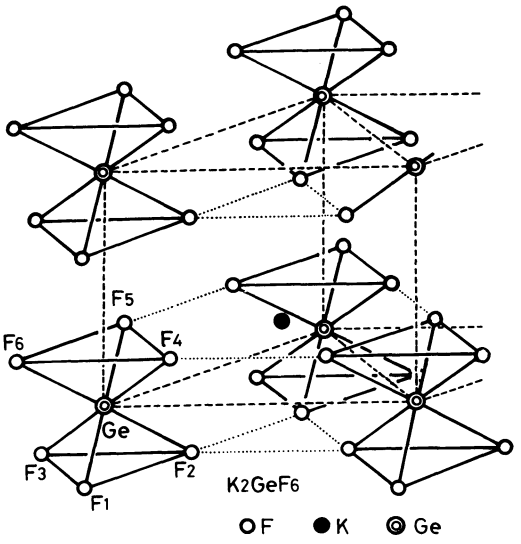

Fig. 2. Structure of K_2GeF_6 and K_2SnF_6. After Ref. 5.

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anions in these crystals are crystallographically equivalent. Since MF_6^{2-} ions form an approximately regular octahedron, the electron distribution in the M-F bond must be close to the axial symmetry. Therefore, axially symmetric chemical-shift tensors at the F atoms may be expected.

Experimental Results and Discussion

1. Spectrometer. Measurements were made by a home-built spectrometer which operates at 40 MHz (suitable for ^{19}F resonance at 1 T). The MREV-8[6] pulse sequence was employed to obtain the high-resolution spectrum in the solid. The shortest interval between pulses was chosen as 6.7 μs, and the optimum resolution of the spectrometer was about 8 ppm (300 Hz). The details of the spectrometer, its operation, and the data-processing procedure have been described elsewhere.[7]

2. Potassium Hexafluorosilicate, K_2SiF_6.

i) Preparation and Measurements: Powdered K_2SiF_6 as purchased from the Nakarai Chemical Co., Ltd., was used for multiple-pulse NMR measurements at 300 and 77 K. The time-domain signals were accumulated 20 times and then Fourier-transformed to obtain a spectrum. The spectra thus obtained are shown in Fig. 3. The spectrum at 300 K has the half-height-width of 30 ppm (1.2 kHz) and does not appear to have any anisotropy. The line-width at 77 K is larger than that at 300 K, and a small additional hump appears on the high-field side.

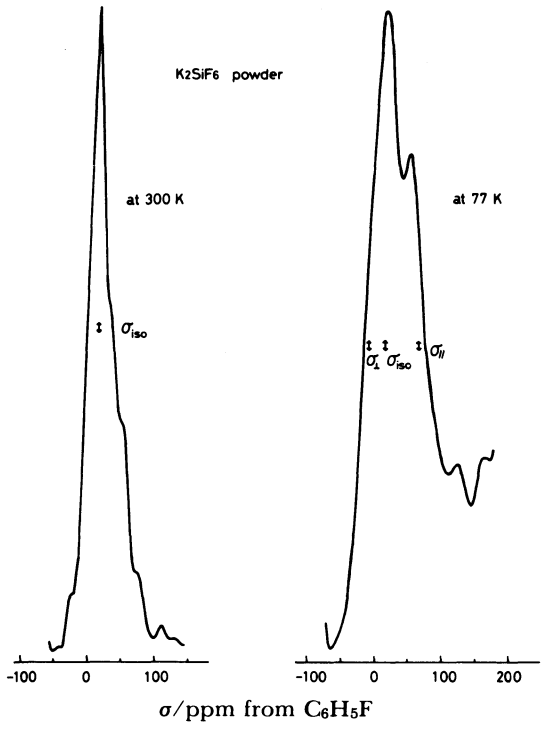

Fig. 3. High-resolution NMR spectra of ^{19}F in powdered K_2SiF_6 at 300 and 77 K. The reference material for the chemical shift is liquid C_6H_5F.

ii) Determination of Chemical-Shift Tensor: The spin-lattice relaxation time of ^{19}F was measured in the temperature range between 77 and 973 K by Moskvich et al.[8] According to them, the correlation time τ_c for the isotropic reorientation of SiF_6^{2-} is about 10^{-6} s at 300 K; therefore, it can be expected that this spherical reorientation will completely average the anisotropy of the chemical-shielding tensor of the ^{19}F nuclei. In fact, the spectrum at 300 K in the present work consists of a single, relatively narrow peak (shown in Fig. 3), which can be explained by such an averaging effect. The value of σ_{av} (isotropically averaged value) obtained is 16±5 ppm relative to the ^{19}F resonance in liquid C_6H_5F.

The spectrum at 77 K shown in Fig. 3 is different from the typical pattern for a rigid lattice: there is a small hump on the high-field side. The overall reorientation of SiF_6^{2-} will affect the line shape to some extent. Thus, Spiess[9] calculated the powder patterns for trigonal bipyramidal, tetrahedral, and octahedral molecules with an axially symmetric shielding tensor in the presence of a certain molecular reorientation in each case. He showed, based on the sudden-jump model, that a small hump may appear as the reorientational correlation time of the molecule approaches the inverse of the magnitude of the chemical-shift anisotropy. The powder pattern of K_2SiF_6 at 77 K was analysed according to the jump model; the chemical-shift anisotropy was estimated to be about 3 kHz, and the correlation time, to be about 3.3×10^{-3} s. The principal values of the shielding tensor were then determined as follows: $\sigma_{33}=66\pm5$ ppm and $\sigma_{22}=\sigma_{11}=-9\pm5$ ppm from liquid C_6H_5F ($\sigma_{33}\geqq\sigma_{22}\geqq\sigma_{11}$).

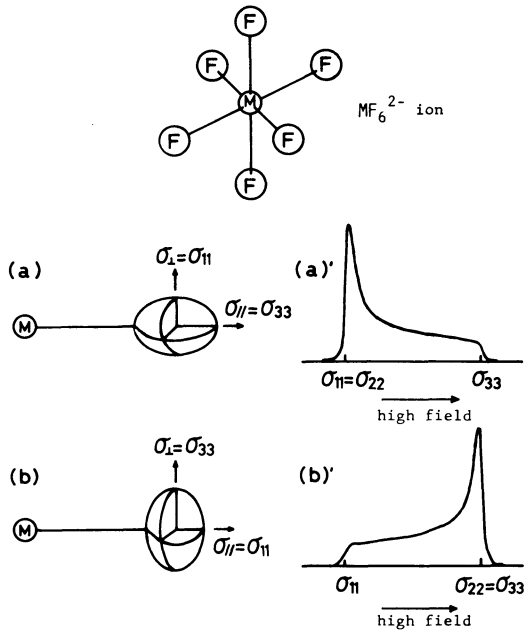

Fig. 4. Axially symmetric shielding tensor models and their powder patterns.

The SiF_6^{2-} ion forms a regular octahedron in the crystal;[4] therefore, the chemical-shielding tensor should be axially symmetric about the Si–F bond. In the case of an atom which forms a single bond, there are two possibilities of axially symmetric shielding tensors, as is shown in Fig. 4. In the **a** type, the maximum shielding direction is along the Si–F bond; in this case, the powder pattern of the **a′** type is obtained. In the case of the **b** type, the least shielded direction is along the Si–F bond, and so the powder pattern should be of the **b′** type. The analysis of the powder pattern of K_2SiF_6 indicates that the shielding tensor in this compound belongs to the **a** type. Therefore, its most shielded direction is along the Si–F bond, and the value of the chemical shift is 66 ppm. Its least shielded direction, on the other hand, is perpendicular to the Si–F bond, and its chemical shift is −9 ppm. The chemical shift of SiF_6^{2-} in a solution is 12 ppm,[2] slightly smaller than the isotropically averaged value in a solid (16 ppm) at room temperature.

3. Potassium Hexafluorogermanate, K_2GeF_6.

i) Preparation and Measurements: A colorless, transparent single crystal in the shape of a hexagonal plate was obtained by the slow evaporation at 30 °C of a solution of GeO_2 and KF in a stoichiometric ratio in 47% hydrofluoric acid. The crystal is of a trigonal symmetry, D_{3d}^3, with $Z=1$, and the C_3 axis of the GeF_6^{2-} ion is parallel to the crystallographic C axis[5] (see Fig. 2). The GeF_6^{2-} ion has the shape of a nearly regular octahedron, and so all the fluorines in the anion may be regarded as having nearly axially symmetric shielding tensors. Therefore, a pair of lines with the intensity ratio of 2:1 may be expected if the Zeeman field is rotated in the plane which is defined by the F_5, Ge, and F_1 atoms and the C_3 axis of the anion (see Fig. 2). A typical example of the spectrum at 300 K is shown in Fig. 5. The time-domain signals were accumulated 20 times at every 1800 s and then Fourier-transformed. When the Zeeman field was rotated in the above-mentioned plane of the crystal, the rotational patterns shown in Fig. 6 were obtained at 300 K. The line labelled by A is about twice as strong as the B line.

ii) Determination of the Chemical-Shift Tensor: From the ^{19}F second moment measured as a function of the temperature, Sergienko et al.[10] saw no sign of the reorientation of the GeF_6 anion, not even at 300 K. Therefore, we can use the rotational pattern of Fig. 6 to derive the rigid-lattice values of the shielding tensor components of ^{19}F. The dotted lines in Fig. 6 show the theoretical angular dependence of the shielding components on the assumption of the axially symmetric shielding tensor. The maximum point of the B curve (low-intensity line) corresponds to a Ge–F bond direction; that is, at this orientation the F_1–Ge–F_5 bond (see Fig. 2) is parallel to the Zeeman field. At the same orientation of the Zeeman field, the A curve (high intensity) has a minimum which indicates that the Zeeman field is perpendicular to both F_2–Ge–F_6 and F_3–Ge–F_4 bonds. Therefore, much as in the case of K_2SiF_6, the most shielded direction is along the Ge–F bond, while the least shielded direction is perpendicular to the Ge–F bond. The

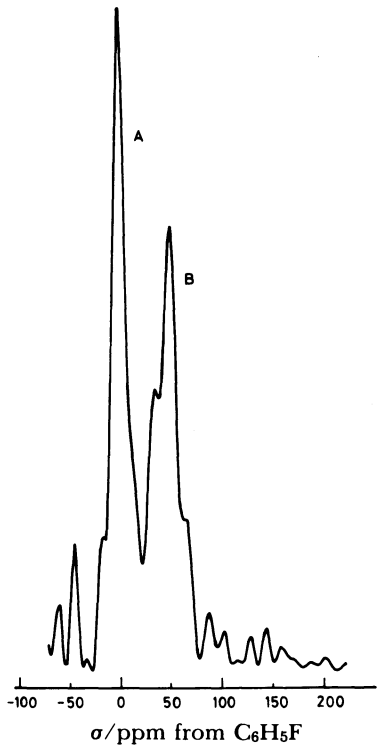

Fig. 5. ^{19}F NMR spectrum obtained by the Fourier transform of FID. The spectrum corresponds to the orientation, a* of Fig. 6.

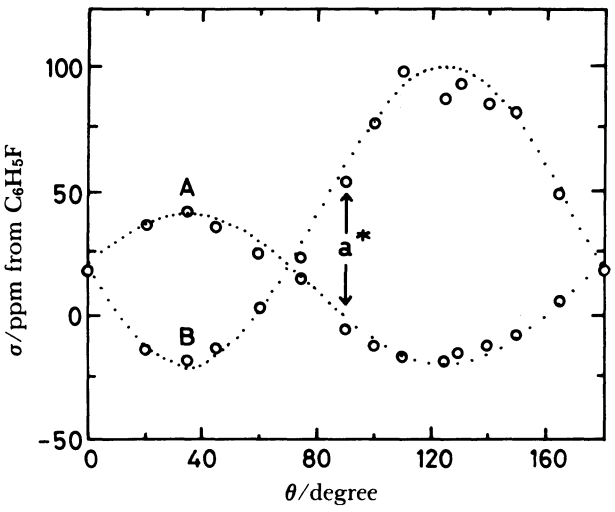

Fig. 6. Angular dependence of the ^{19}F chemical shifts of K_2GeF_6 single crystal. The pattern was obtained when the Zeeman field was rotated in the plane which is defined by F_5, Ge, and F_1 atoms and the C_3 axis (see Fig. 2). The angle θ is measured from the direction of the C_3 axis.

values of the shielding tensor components were thus determined as follows: $\sigma_{33}=99\pm3$ ppm and $\sigma_{22}=\sigma_{11}=-20\pm3$ ppm from liquid C_6H_5F. The isotropically averaged value is 19 ppm, significantly larger than that of ^{19}F in GeF_6^{2-} in solution (7 ppm).[2]

4. Potassium Hexafluorostannate, K_2SnF_6.

i) Preparation and Measurements: A K_2SnF_6 single crystal was obtained by the slow evaporation at 30 °C of a solution of $K_2Sn(OH)_6$ in 47% hydrofluoric acid. The crystal belongs to a trigonal system, and the site symmetry of Sn is D_{3d}.[5]

Multiple pulse measurements were made on the single crystal at 300 K in a manner similar to the case of K_2GeF_6. Contrary to the case of K_2GeF_6, no angular dependence of the shielding tensor was detected at 300 K, which indicates that the rapid molecular reorientation averages out the anisotropy in the shielding tensor, as in the case of K_2SiF_6. Then we carried out experiments on the powdered specimen at 300 and 77 K and reproduced the resulting spectra in Fig. 7. The spectrum at 300 K is a single, approximately symmetric peak, whereas the spectrum at 77 K corresponds to a typical powder pattern, involving some degree of anisotropy.

ii) Determination of the Chemical-Shift Tensor: The powder pattern at 300 K gives a motionally averaged, isotropic shielding with a σ_{av} value of 83 ± 5 ppm. The analysis of the powder pattern at 77 K, on the other hand, gives $\sigma_{33}=183\pm5$ ppm and $\sigma_{22}=\sigma_{11}=33\pm5$ ppm by assuming an axially symmetric shielding tensor. The most shielded direction is along the Sn–F bond, while the least shielded direction is perpendicular to the Sn–F bond. The averaged value, 83 ppm, is very different from that in SnF_6^{2-} in a solution (40 ppm).[2]

5. Discussion. Among the series of compounds of Group IV_b elements (C, Si, Ge, Sn, and Pb), silicon compounds show unusual behavior in several magnetic resonance properties, e.g., NMR chemical shifts[2,11] and NQR frequencies,[1] which reflect the electronic structures of atoms or molecules. The values of the chemical shielding of the compounds in this study are summarized in Fig. 8. To obtain some insight into the electronic structure of the molecules, the theory of Karplus and Das[12] will be used. The chemical-shift tensor consists of two contributions;

$$\sigma = \sigma^d + \sigma^p \tag{1}$$

where σ^d and σ^p are, respectively, the diamagnetic and paramagnetic parts of the chemical-shift tensor. Since it is the paramagnetic contribution that mainly gives rise to the experimentally observed variations in the chemical shifts of ^{13}C, ^{19}F, etc.,[12] only the paramagnetic part will be considered in investigating the electronic structure. According to the theory of Karplus and Das, the axially symmetric chemical-shift tensor for the atoms in this study can be given as follows:

$$\sigma_{//}^p = (3/2)\sigma_o(2\rho_\perp - \rho_\perp^2) \tag{2}$$

for the component along the M–F bond and

$$\sigma_\perp^p = (3/2)\sigma_o[\rho_\perp + (1-\rho_\perp)\varepsilon] \tag{3}$$

for the component perpendicular to the M–F bond, where σ_o is a semiempirical parameter, where $\rho_\perp$ is the π-bond character, and where

$$\varepsilon = 1 + IS - I - S. \tag{4}$$

I and S are the ionic character and the degree of sp hybridization respectively.

The $\sigma_{//}$ component increases regularly from K_2SiF_6 to K_2SnF_6, as is shown in Fig. 8. On the other hand, the $\sigma_\perp$ component of K_2SiF_6 seems to be anomalously large, presumably reflecting the anomalous character of the Si–F bond. Since $\sigma_{//}$ increases on going from K_2SiF_6 to K_2SnF_6, $|\sigma_{//}^p|$ must decrease in the same order. According to Eq. 2, it is concluded that the π-bond character, $\rho_\perp$, decreases regularly from K_2SiF_6 to K_2SnF_6. Such a tendency may be interpreted by

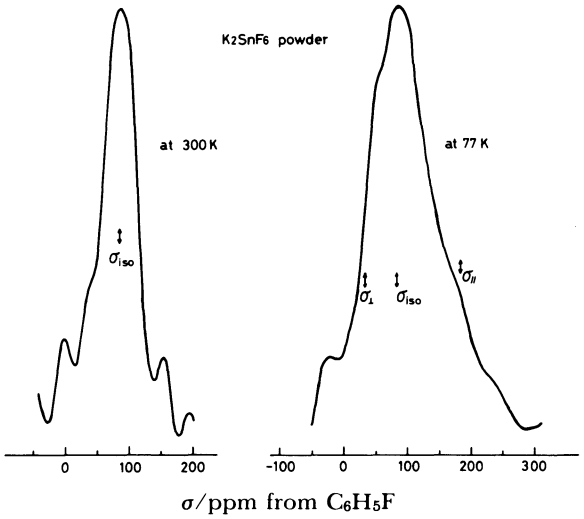

Fig. 7. Powder pattern of ^{19}F NMR in K_2SnF_6.

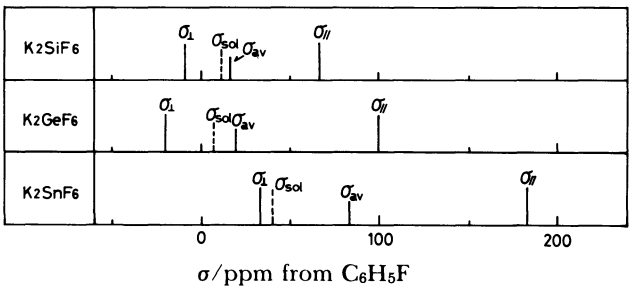

Fig. 8. Pictorial representation of the chemical shift tensor elements in K_2MF_6 (M=Si, Ge, and Sn) compounds. σ_{sol} is isotropic value in solution after Ref. 2.

introducing the concept of π-backbonding: the Group IV_b elements employ two d-orbitals in the octahedral d^2sp^3 hybridized orbitals for the framework of the MF_6^{2-} complex, and so the three remaining d-orbitals have the capability of forming π-bonding with orbitals of the ligand atoms. Through this π-bonding, partial electrons will be transferred from the ligands to the center atom. As $\rho_\perp$ is largest in the Si complex in the present series, we may consider that the π-backbonding is the strongest in K_2SiF_6.

An anomalously large $\sigma_\perp$ value was derived for SiF_6^{2-} compared with the other two compounds. According to Eq. 3, ε should be very small, so small as to cancel the effect of the large $\rho_\perp$ value in SiF_6^{2-}, which implies that the ionic or hybridyzation term in Eq. 4 should be large. Sanderson[13] and Hargittai and Bliefert[14] reexamined the electronegativity scale and showed that the electronegativity decreases in this order; C>Ge>Sn>Si. The anomalously large $\sigma_\perp$ value may be attributed to the high ionic character of the Si–F bond.

It may be noted in Fig. 8 that the difference between the trace of the chemical-shift tensor in the solid state, σ_{av}, and the isotropic chemical shift in a solution, σ_{sol}, is largest in K_2SnF_6. The large value shows that there is a large difference in the electronic structure of the MF_6^{2-} ion between the solid and liquid states. It is considered that the affinity of SnF_6^{2-} to water molecules in a solution is strongest, since the solubility of K_2SnF_6 is largest, and that this interaction causes a change in the electronic distribution in the SnF_6^{2-} anion.

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