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A determination of the Ti–F bond distance in K_2TiF_6 by nuclear magnetic resonance.

By James A. Ibers and C. H. Holm, *Shell Development Company, Emeryville, California, U.S.A.*

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It is now well established that structural information may be derived from nuclear magnetic resonance absorption spectra. (As a general reference we give Andrew (1955).) For very simple systems of rigid nuclei the shape of the absorption curve may be calculated as a function of the atomic arrangement and may be compared with the observed shape. For more complicated systems this calculation is both difficult and unrewarding. However, Van Vleck (1948) has shown that the moments of the absorption spectrum may be readily calculated, even for complicated systems. For the case of rigid nuclei the following expression may be derived from Van Vleck's results:

$$S_j = \tfrac{3}{4} I_j(I_j+1)(v_j h/H_0)^2 \sum_{j' \neq j} (3\cos^2\theta_{jj'}-1)^2 r_{jj'}^{-6}$$
$$+ \tfrac{1}{3} \sum_k I_k(I_k+1)(v_k h/H_0)^2 (3\cos^2\theta_{jk}-1)^2 r_{jk}^{-6}\,. \quad (1)$$

Here S_j is the second moment of the absorption spectrum for nuclei j. The first summation represents the contribution to the second moment of nuclei j of spin $I_j = \frac{1}{2}$*; the second summation represents the contribution of other nuclei k of spin I_k. v_j and v_k are the resonance frequencies corresponding to nuclei j and k at an applied uniform field $\mathbf{H}$ of magnitude H_0. The internuclear distance between nuclei m and n is $\mathbf{r}_{mn}$. θ_{mn} is the angle between $\mathbf{r}_{mn}$ and $\mathbf{H}$. A value of the second moment, and hence information about the sums of the inverse sixth powers of the internuclear distances, is thus obtained for each orientation of the single crystal relative to the field direction. In order to solve the structure it is useful, if not essential, to have a model in mind, for a series of equations of the form of (1) has no unique solution in general. For this reason the second-moment technique may be considered most valuable when from other methods the atomic arrangement is known except for precise information on the location of a few nuclear species. Since of the more common nuclei hydrogen and fluorine have the largest nuclear magnetic resonance frequencies at a given field, this technique is particularly valuable for the location of these atoms in otherwise well-defined structures. The determination of the hydrogen positions in NH_4Cl by Bersohn & Gutowsky (1954) from the proton absorption spectrum and equation (1) is an example of such an application of the second-moment technique.

If a powder specimen is used all terms of the type $(3\cos^2\theta_{mn}-1)^2$ in (1) average to $\frac{4}{5}$, and the calculations are simplified somewhat. At the same time the complexity of the structures which can be studied is severely limited, for in principle the single value of the second moment which is now obtained will yield only one structure parameter. In actual practice, however, this need not be the case. Thus, we will show below that the second moment obtained from the F^{19} resonance absorption spectrum of K_2TiF_6 powder can be made to yield a reasonably accurate value for the Ti–F distance, even though a complete description of the structure of K_2TiF_6 requires the determination of three parameters.

K_2TiF_6 was prepared by the addition of KF to an aqueous solution of HF containing dissolved TiO_2. The thin hexagonal plates of K_2TiF_6 which crystallized out upon cooling the solution were dried in a vacuum desiccator. The F^{19} magnetic resonance absorption spectrum was obtained using a Varian V-4200A nuclear magnetic resonance spectrometer at a frequency of about 14 mc.sec.$^{-1}$ and an associated V-4012A electromagnet at a field of about 3500 gauss. The spectrum was observed at two temperatures, 20° C. and −94° C. If K_2TiF_6 exhibits significant thermal vibrations at room temperature, then we would expect the spectrum at −94° C. to be broader than that at 20° C., and hence the second moment to be higher. Actually the second moment is about 5% higher at −94° C. About 2% of this increase may be accounted for by the expected decrease in lattice constants; the remaining 3% difference is not significant when one considers the errors of measurement. We are therefore justified in assuming that K_2TiF_6 is essentially rigid at room temperature, and we may then use equation (1), which is strictly valid only for rigid solids. Incidentally, the close agreement between the second moments at −94° C. and 20° C. is reasonable evidence that K_2TiF_6 undergoes no transitions within that temperature range. The second moment obtained from a weighted average of ten measurements is $6{\cdot}39 \pm 0{\cdot}13$ gauss^2.

For K_2TiF_6 powder, equation (1) reduces to:

$$S_F = 317{\cdot}136 \sum_{F'} r_{F-F'}^{-6} + 3{\cdot}910 \sum_{Ti} r_{Ti-F}^{-6} + 1{\cdot}649 \sum_{K} r_{K-F}^{-6} \quad (2)$$

Because the Ti–F and K–F contributions to the second moment are very small and because the structure by analogy with K_2GeF_6 (Hoard & Vincent, 1939) may be assumed to be quite simple, it would be possible from geometrical considerations and the observed second moment alone to derive a reasonably accurate Ti–F distance. This approach has not been used since X-ray data are available. The following information is given by Siegel (1952) or may be derived from his X-ray results:

K_2TiF_6: trigonal. Hexagonal axes $a = 5{\cdot}715$, $c = 4{\cdot}656$ Å. $Z = 1$. D_{3d}^3–$P\bar{3}m1$.
Ti in (*a*);
K in (*d*) with $z' = 0{\cdot}700 \pm 0{\cdot}004$;
F in (*i*) with $x = 0{\cdot}156 \pm 0{\cdot}003$, $z = 0{\cdot}244 \pm 0{\cdot}004$.
Ti–F = $1{\cdot}917 \pm 0{\cdot}026$ Å; intra F–F in the TiF_6^- group $2{\cdot}747 \pm 0{\cdot}038$, $2{\cdot}675 \pm 0{\cdot}038$ Å.

K_2TiF_6 has the K_2GeF_6 structure (Hoard & Vincent, 1939), and may be described roughly as a distorted cubic ammonium chloroplatinate arrangement of K^+ and TiF_6^- ions.

In order to determine the Ti–F distance we assume the potassium positions given by Siegel, and we further assume that the TiF_6^- octahedron is perfectly symme-

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* Equation (1) is valid for nuclei of spin greater than $\frac{1}{2}$, but quadrupole effects, which are most difficult to take into account, also contribute to the absorption spectra obtained from such nuclei.

tric. This latter assumption requires that $z = (3/2)^{\frac{1}{2}}(a/c)x$, and reduces the determination of the Ti–F distance to the determination of the single parameter x. For the calculation of the second moment all F–F internuclear distances out to 10 Å and all K–F and Ti–F distances out to 5 Å as a function of x were calculated for the symmetric model; the sums in equation (2) over distances longer than these were obtained by integration. The following value of x and the distances corresponding to it were calculated from the observed second moment:

$$x = 0{\cdot}1580 \pm 0{\cdot}0016 \quad (z = 0{\cdot}2376 \pm 0{\cdot}0024);$$
$$\text{Ti–F} = 1{\cdot}916 \pm 0{\cdot}020\ \text{Å},\quad \text{F–F} = 2{\cdot}709 \pm 0{\cdot}028\ \text{Å}\,.$$

The contributions of the various terms in (2) to the moment are F–F 98·5%, Ti–F 1·3%, and K–F 0·2%.

The limits of error given above are those which arise from the errors in the measurement of the second moment, and do not reflect the errors due to the assumption of a symmetric model. It is reasonable to ask how large these latter errors might be. Siegel's structure corresponds to a calculated second moment of 6·48 gauss^2. The symmetric model which corresponds to this moment has Ti–F = 1·904 Å, some 0·013 Å shorter than Siegel's value. It should be noted, however, that the two F–F distances derived by Siegel are not significantly different on the basis of the usual statistical tests (Cruickshank & Robertson, 1953); hence, the symmetric model cannot be eliminated on the basis of Siegel's results. It is thus unreasonable to require that the Ti–F distance derived above should be corrected because it is based on the symmetric model. Moreover, the Ti–F distances of 1·917± 0·026 Å (X-ray) and 1·916±0·020 Å (n.m.r.) are in excellent agreement.

The value of the Ti–F distance derived above from the nuclear magnetic resonance data is believed to be reasonably accurate and precise. What is perhaps more important, it was obtained with considerably less time and effort than would be required to obtain similar precision from X-ray methods. Thus, nuclear magnetic resonance techniques are powerful ones for the elucidation of certain, rather specific, structural information. The case of K_2TiF_6 is perhaps atypical, for the structure is so simple that the Ti–F distance could have been derived from the second moment without the aid of the X-ray information. In general, however, this is not the case, and it must be emphasized that nuclear magnetic resonance techniques are essentially complementary with X-ray techniques.

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The unit cell and space group of the compound $TiNb_2O_7$.*

By P. Dyson,† *Research Laboratories of The General Electric Company Limited, Wembley, England*

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The compound $TiNb_2O_7$ was first recorded by Roth & Coughanour (1955) in a paper dealing with phase equilibrium in the system TiO_2–Nb_2O_5. Its existence has been confirmed in the course of a similar investigation in these Laboratories.

When fired at 1350° C., pressed blocks of the mixed oxides, of appropriate composition, yield a somewhat porous, pale yellow mass of crystals of the compound, up to $\frac{1}{4}$ mm. in size.

The ease of crushing indicates a hardness of about 4 on Mohs scale.

There are two good cleavages which make a large angle with one another. On account of this, crushed fragments often show an elongated prismatic form parallel to the edge common to the cleavage traces. Between crossed nicols the extinction is parallel to this edge. The refractive indices are much higher than 1·74 (methylene iodide) and the birefringence, in sections parallel to a cleavage direction, is low.

The above observations indicate that the symmetry is at least monoclinic, with the b axis parallel to the cleavage traces.

Single-crystal rotation and zero- and first-layer Weissenberg photographs of a cleavage fragment rotated about the b axis give the following dimensions for the unit cell:

$$a_0 = 11{\cdot}9,\ b_0 = 3{\cdot}77,\ c_0 = 10{\cdot}1\ \text{Å},\ \beta = 120°\,.$$

The Weissenberg photographs show no systematic absences of reflexions. The space group is thus one of three, namely $P2$, Pm or $P2/m$.

An approximate density measurement suggested 4·38 ($TiNb_2O_7$) per unit cell. If the true value is assumed to be 4 ($TiNb_2O_7$), the calculated density is 5·89 g.cm.$^{-3}$.

The dielectric constant shows no anomalies with change of temperature and does not establish the presence or absence of a centre of symmetry.

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* Communication No. 710 from the Staff of the Research Laboratories of The General Electric Company Limited, Wembley, England.

† Present address: A.O. Nigeria Limited, P.O. Bukuru, Northern Nigeria.