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The Crystal Structure of K_2TiF_6

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K_2TiF_6 is trigonal and the structure is of the K_2GeF_6 type. The unit cell dimensions are $a = 5{\cdot}715 \pm 0{\cdot}002$, $c = 4{\cdot}656 \pm 0{\cdot}001$ Å.

Each titanium atom is linked to six fluorine atoms at the corners of a distorted octahedron, with Ti–F = 1·91 Å. This leads to a Ti^{+4} radius of 0·58 Å. Each potassium is bonded to twelve fluorine atoms, of which six are at a distance of 2·87 Å, three at 2·75 Å, and three at 3·08 Å.

Introduction

Crystals of K_2TiF_6 were prepared by dissolving TiO_2 in HF and precipitating the desired salt by the addition of KHF_2. Crystals so prepared always formed as hexagonal plates with the flat surface parallel with $00l$.

Interpretation of a powder pattern of K_2TiF_6 indicated that the structure is based upon a hexagonal cell. Measurements with a recording spectrometer resulted in the following cell constants:

$$a = 5{\cdot}715 \pm 0{\cdot}002,\quad c = 4{\cdot}656 \pm 0{\cdot}001 \text{ Å}.$$

The observed density, ϱ, was found to be 3·07 g.cm.$^{-3}$. With the unit-cell dimensions given above, this leads to one molecule per unit cell. The calculated density is therefore $\varrho = 3{\cdot}01$ g.cm.$^{-3}$.

K_2TiF_6 is trigonal and belongs to the space group D^3_{3d}–$C\bar{3}m$. With one molecule in the unit cell, we may place atoms in the following positions:

1 Ti in $0, 0, 0$.
2 K in $\frac{1}{3}, \frac{2}{3}, u;\ \frac{2}{3}, \frac{1}{3}, \bar{u}$.
6 F in $x, \bar{x}, z;\ x, 2x, z;\ 2\bar{x}, \bar{x}, z;$
$\bar{x}, x, \bar{z};\ \bar{x}, 2\bar{x}, \bar{z};\ 2x, x, \bar{z}$.

The structure determination

Single-crystal photographs were obtained with a Weissenberg goniometer. As the crystals were flat plates parallel with $00l$, only the a axis could serve as the rotation axis. However, using data obtained from four layer lines, sufficient information was available for the determination of the atomic parameters with reasonable accuracy.

The tabular character of the crystal introduced considerable focusing of the $00l$ reflections, including those arising from planes approximately parallel with $00l$. Furthermore, absorption became very high in certain directions. As a consequence, the parameters

Table 1. *Observed and calculated structure factors*

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
001	22·0	7·4	311	5·0	2·4	$32\bar{1}$	0	0·7
002	46·0	−45·0	$31\bar{1}$	30·0	24·0	322	0	0·6
003	25·0	25·0	213	4·3	− 0·7	$32\bar{2}$	14·0	15·0
004	33·0	34·0	$21\bar{3}$	0	0·3	124	17·0	− 7·2
005	2·8	− 4·0	312	23·0	21·0	$12\bar{4}$	27·0	19·0
006	8·1	23·0	$31\bar{2}$	0	3·2	323	0	− 4·1
			114	11·0	7·6	$32\bar{3}$	0	7·2
201	37·0	−32·0	$11\bar{4}$	9·3	7·6	125	21·0	19·0
$20\bar{1}$	53·0	68·0	412	0	1·0	$12\bar{5}$	13·0	11·0
102	0	1·5	$41\bar{2}$	0	0·5			
$10\bar{2}$	27·0	28·0	413	23·0	16·0	031	11·0	12·0
301	0	− 2·5	$41\bar{3}$	27·0	24·0	$03\bar{1}$	1·8	− 2·5
$30\bar{1}$	12·0	13·0	511	18·0	18·0	032	0	3·6
302	0	2·7	$51\bar{1}$	0	2·0	$03\bar{2}$	0	2·7
$30\bar{2}$	0	3·6				131	19·0	24·0
401	33·0	42·0	021	63·0	68·0	$13\bar{1}$	2·3	6·6
$40\bar{1}$	16·0	−18·0	$02\bar{1}$	33·0	−36·0	034	5·9	7·7
			121	14·0	8·7	$03\bar{4}$	8·8	8·2
011	11·0	−16·0	$12\bar{1}$	29·0	23·0	331	0	3·5
$01\bar{1}$	27·0	34·0	122	33·0	29·0	$33\bar{1}$	0	3·5
112	5·2	3·6	$12\bar{2}$	0	8·2	332	0	− 0·7
$11\bar{2}$	3·0	3·6	221	11·0	5·4	$33\bar{2}$	0	− 0·7
211	29·0	22·0	$22\bar{1}$	10·0	5·4	234	0	0
$21\bar{1}$	12·0	8·6	222	15·0	−23·0	$23\bar{4}$	22·0	23·0
212	3·6	7·2	$22\bar{2}$	13·0	−23·0	333	21·0	19·0
$21\bar{2}$	27·0	30·0	321	27·0	23·0	$33\bar{3}$	20·0	19·0

were established by considering the ratio of the intensities, $I_{hkl}/I_{h\bar{k}\bar{l}}$, thereby reducing errors arising from absorption effects.

The x coordinate was obtained by considering those reflections $hk0$ for which $I_{hk0} = 0$. The determination of u and z then involved essentially a trial-and-error procedure. However, using reasonable K–F distances, these parameters could be determined with a minimum of effort. The final values are: $u = 0{\cdot}700 \pm 0{\cdot}004$, $x = 0{\cdot}156 \pm 0{\cdot}003$, and $z = 0{\cdot}244 \pm 0{\cdot}004$. A comparison between observed and calculated structure factors is given in Table 1. Absorption and temperature corrections are not included.

Results

The resulting structure shows each titanium atom to be linked to six fluorine atoms at the corners of a distorted octahedron. The interionic distance is Ti–6F = 1·91 Å. With the value of 1·33 Å for the F^- radius (Zachariasen, 1950) we obtain 0·58 Å for the Ti^{+4} radius, which is in excellent agreement with the value 0·60 Å reported by Zachariasen (1950). Each potassium atom is bonded to twelve fluorine atoms, of which six are at a distance of 2·87 Å, three at 2·75 Å, and three at 3·08 Å, the average distance being 2·89 Å. This distance may be compared with the value of 2·85 Å for K^+–F^- deduced from the ionic radii of Zachariasen. The agreement is very satisfactory.

This structure is one of several now reported which are of the K_2GeF_6 type (Hoard & Vincent, 1939).

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A Neutron-Diffraction Study of Magnesium Aluminium Oxide

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The neutron-diffraction pattern of spinel, $MgAl_2O_4$, demonstrates that the cationic arrangement corresponds closely with the so-called 'normal' structure, the scattering amplitudes of Mg and Al being sufficiently different to distinguish this from the 'inverse' structure. The oxygen parameter u is 0·387.

Introduction

Many metal oxides of the type XY_2O_4 have the 'spinel' structure, so-called after the mineral spinel $MgAl_2O_4$, which was first investigated with X-rays by Bragg (1915) and by Nishikawa (1915). The structure may be considered to consist of an arrangement of close-packed oxygen ions with two types of interstices for the metal ions. The unit cell, which contains eight molecules, includes eight metal positions (A sites) tetrahedrally co-ordinated by oxygen and sixteen (B sites) octahedrally co-ordinated. In the simplest arrangement of the cations the eight X ions occupy the A sites and the sixteen Y ions the B sites. This arrangement is usually termed 'normal' in contrast to the so-called 'inverse' structure in which the A sites are occupied by eight of the Y ions with the B sites filled by the X ions and remaining Y ions distributed at random. It was shown by Barth & Posnjak (1932), who first drew this distinction, that X-ray intensity measurements could distinguish the two cases if the scattering powers of the X and Y ions were sufficiently different. For spinel itself, magnesium aluminium oxide, the scattering factors for Mg^{++} and Al^{+++} are too nearly equal for any decision to be made. In the case of neutron diffraction, however, the scattering cross-section of a magnesium nucleus is sufficiently greater than that of aluminium to suggest that a distinction should be possible. Before describing an experimental investigation of this point it is recalled, as emphasized by Verwey & Heilmann (1947), that the 'normal' and 'inverse' arrangements are merely the two extremes of a continuous range of distributions which satisfy the spinel symmetry.

Experimental measurements

In the absence of a suitable single crystal of pure $MgAl_2O_4$ the measurements were made by powder-diffraction methods using a sample prepared in the laboratory of the Royal College of Science by Mrs A. E. Carter. A mixture of partly hydrated Al_2O_3 and $MgCO_3$ was fired at 1400° C. for 15 hr., followed by