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X-Ray Diffraction Studies of Some Transition Metal Hexafluorides[1]

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Crystallographic studies are presented for the transition metal hexafluorides MoF_6, TcF_6, RuF_6, RhF_6, WF_6, ReF_6, OsF_6, IrF_6, and PtF_6. Each exhibits a cubic modification near room temperature and a phase of lower symmetry, probably orthorhombic, at reduced temperatures. Unit cell sizes for both phases as well as transition temperatures are given. X-Ray results are presented for ReF_7, which also exhibits a cubic phase at room temperature and a second modification at a very low temperature.

Introduction

Hexafluorides of a number of transition metals have been prepared, and details concerning the chemistry and physical properties of many of these compounds have been described elsewhere.[2-14]

We wish to report here the results of X-ray diffraction studies of MoF_6, TcF_6, RuF_6, RhF_6, WF_6, ReF_6, OsF_6, IrF_6, and PtF_6. In addition, some X-ray data will be furnished for ReF_7.

Each hexafluoride near room temperature can be indexed on the basis of a body-centered cubic cell. However, at reduced temperatures, a phase transition to a lower symmetry occurs. The similarity of pattern types is considered an indication that all compositions belonging to a specific phase are isostructural. ReF_7 shows the unexpected result that it can also be indexed as body-centered cubic at room temperature, and furthermore it transforms to a phase of lower symmetry at reduced temperatures.

Experimental Procedure

A capillary containing the sample was mounted in a commercial powder camera which had been modified to permit use of a cooling nozzle as described by Post, *et al.*[15]

Nitrogen, cooled and dried, was passed over the sample capillary by means of a silvered vacuum-walled tube. An outer jet of uncooled nitrogen provided two gas–gas interfaces which eliminate icing. Temperature control was established by use of a heater and proper flow rate for the nitrogen gas. Temperatures were measured in a conventional manner with a thermocouple placed close to the sample.

Reference to Table III shows that the temperature range over which the cubic phase is stable is very narrow. However, the vapor pressure is quite high within this range, and, as a result, slight temperature gradients within the sample capillary will cause crystals to grow, disappear, and reappear elsewhere. Diffraction patterns produced from such samples give nonuniform maxima. The patterns can be improved by allowing the sample to undergo a solid–solid or solid–liquid phase transition frequently by changing the temperature. Upon recooling, smaller crystallites with random orientations will form.

In order to improve the intensity distribution still further, a translation was superimposed on the sample rotation. A device for performing this has been described.[16] Data for all compositions were obtained with copper radiation.

Results and Discussion

The high-temperature phase was indexed on the basis of a body-centered cubic cell. Any modifications of the symmetry arising from the effects of the light fluorine atoms may be obscured by the high cation absorption and the poor intensity distribution within a line.

Generally, the diffraction intensities dropped substantially near $\sin^2 \theta = 0.4$; however, because of the high sample absorption, it was necessary to derive the cell constants by extrapolation of the data to $\sin^2 \theta = 1.0$. Unit cell sizes and calculated X-ray densities for the cubic modification are presented in Table I.

Single crystals of the low-temperature modification could be grown but not isolated. For this reason, the true symmetry of this phase was not determined uniquely by X-ray methods. However, powder patterns of the low-temperature form appeared to be similar to that of UF_6, which Hoard and Stroupe[17] reported as orthorhombic, with $a = 9.900$ A, $b = 8.962$ A, and $c = 5.207$ A. If structural similarity to UF_6 is assumed, a set of orthorhombic constants and densities can be derived as shown in Table II. Here also, the unit cell sizes have been obtained by extrapolation of values to $\sin^2 \theta = 1.0$. Melting points and phase transition temperatures for the hexafluorides as well as for ReF_7 are presented in Table III.

ReF_7 was found by Malm, Selig, and Fried[4] in the preparation of ReF_6. X-Ray diffraction patterns of the isolated ReF_7 sample showed a body-centered cubic cell for temperatures as low as $-90°$. Studies

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

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TABLE I

HIGH-TEMPERATURE PHASE UNIT CELL SIZES AND CALCULATED DENSITIES

Substance	Temp, °C	Cell constant, A	Calcd density, g/cc (Z = 2)
MoF_6	+5	6.23 ± 0.04	2.88
TcF_6	+10	6.16 ± 0.03	3.02
RuF_6	+25	6.11 ± 0.01	3.13
RhF_6	+25	6.13 ± 0.02	3.13
WF_6	0	6.28 ± 0.02	3.99
ReF_6	+10	6.26 ± 0.02	4.06
OsF_6	+25	6.25 ± 0.02	4.13
IrF_6	+25	6.23 ± 0.02	4.20
PtF_6	+25	6.21 ± 0.02	4.28

TABLE II

LOW-TEMPERATURE PHASE UNIT CELL SIZES AND CALCULATED DENSITIES

Substance	Temp, °C	Cell dimensions, A, to ±0.02			Calcd density, g/cc (Z = 4)
		a	b	c	
MoF_6	−36	9.61	8.75	5.07	3.27 ± 0.03[a]
TcF_6	−19	9.55	8.74	5.02	3.38 ± 0.03
RuF_6	−30	9.44	8.59	4.98	3.50 ± 0.03
RhF_6	−23	9.40	8.54	4.96	3.62 ± 0.03
WF_6	−20	9.68	8.81	5.09	4.56 ± 0.03
ReF_6	−22	9.61	8.76	5.06	4.68 ± 0.03
OsF_6	−21	9.59	8.75	5.04	4.77 ± 0.03
IrF_6	−11	9.58	8.73	5.04	4.82 ± 0.03
PtF_6	−11	9.55	8.71	5.03	4.90 ± 0.03
UF_6	+25	9.900	8.962	5.207	5.061

[a] A density of 3.311 g/cc is obtained by extrapolation of data obtained by He displacement. See D. W. Osborne, F. Schreiner, J. G. Malm, H. Selig, and L. Rochester, *J. Chem. Phys.*, **44,** 2802 (1966). R. Schablaske and B. Tani report (private memorandum, Argonne National Laboratory, Feb 1, 1966) that they indexed a MoF_6 pattern as orthorhombic with a = 9.65 ± 0.02 A, b = 8.68 ± 0.03 A, and c = 5.05 ± 0.02 A In this case, the sample was cooled to −20°.

TABLE III

MELTING POINTS AND TRANSITION TEMPERATURES

Compd	Mp, °C	Transition temp, °C	Compd	Mp, °C	Transition temp, °C
MoF_6	17.4	−9.6	ReF_6	18.5	−3.5
TcF_6	37.0	−5.3	OsF_6	33.2	1.4
RuF_6	54.0	2.5	IrF_6	44.0	−1.2
RhF_6	. . .	. . .	PtF_6	61.3	3.0
WF_6	1.9	−8.5	ReF_7	48.3	−110

at −110 and −133° indicated, however, that a phase change had taken place to a modification of lower symmetry. Cell dimensions and densities of the cubic form as a function of temperature are given in Table IV.

TABLE IV

ReF_7 UNIT CELL SIZE AND DENSITY AS A FUNCTION OF TEMPERATURE; CUBIC PHASE

Temp, °C	Cell constant a_0, A	Calcd density, g/cc	Temp, °C	Cell constant a_0, A	Calcd density, g/cc
+25	6.26 ± 0.02	4.32	−45	6.17 ± 0.01	4.51
−5	6.25 ± 0.02	4.34	−82	6.16 ± 0.01	4.53
−25	6.21 ± 0.02	4.42	−90	6.140 ± 0.004	4.579

ReF_7 exhibits a behavior similar to IF_7, which has been reported by Burbank and Bensey[18] and Burbank.[19] These authors find IF_7 to be body-centered cubic down to −120° with a cell size of 6.28 A. At lower temperatures the symmetry is orthorhombic with a = 8.74 A, b = 8.87 A, and c = 6.14 A at −145°. The relationship between the ReF_7 and IF_7 low-temperature forms has not been established.

Further crystallographic work on any of the hexafluorides will require single crystal methods. It does not seem possible that powder patterns can be improved sufficiently to permit structure determination.

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