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Cerium Oxyfluoride and Its Lattice Structure

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SOME years ago, Klemm and Klein[1] published a note according to which lanthanum oxyfluoride LaOF can be produced by heating a mixture of LaF$_3$ and La$_2$O$_3$ for one hour at 900°C in high vacuum. They found that the new compound crystallizes in a cubic lattice with a lattice constant $a = 5.756 \pm 0.003$A. This lattice constant increases up to 5.82A if an excess of fluorine is dissolved in the LaOF.

In a still unpublished investigation, H. Stintzing at Darmstadt (1942–1944) confirmed these results and extended them by studying also high intensity carbon cores in which fluorides and oxides of the rare earths are used after extensive baking. Diffraction patterns of these cores revealed two lines indicating a cubic lattice with a lattice constant 5.70 ± 0.01A, i.e., somewhat smaller than that of the pure LaOF. While Stintzing assumed that this diminished lattice constant was caused by the participation of cerium in the oxyfluoride lattice, he was not able to find more than traces of two CeOF lines when he started with pure CeF$_3$ and baked it in a rarified atmosphere at high temperatures with or without carbon. He concluded that CeOF was of low stability and that, in contrast to LaF$_3$, CeF$_3$ has little inclination to form CeOF in the presence of oxygen.

Without detailed knowledge of Stintzing's results, a complete report of which has become available only after the main part of our studies had been carried out, we have made extensive x-ray diffraction studies of the rare earth oxides and fluorides in isolated form and in carbon mixtures, after they had been subjected to different heat treatments. The investigation was carried out with a General Electric x-ray diffraction instrument using a copper tube and a camera of 71.6 mm radius. Apparently our resolving power was higher than that of Stintzing as, in contrast to his statement, we could easily resolve the lines of substances with a lattice constant difference of as little as 0.03A. In further contrast to Stintzing who could not discover any graphite lines and only two LaOF lines, we found all the 14 oxyfluoride lines of cerium and lanthanum which are expected theoretically for scattering angles below 120°, in addition to the six strongest graphite lines (in mixtures with graphite) which, being very sharp, could be used as calibration lines. For the purpose of checking this calibration, or whenever graphite was not present or not in sufficient concentration in the samples, small amounts of pure CeO$_2$ or TlCl were added to the substances under investigation. As samples, tiny cylinders of 0 15 to 0.2 mm diameter were used which were made from the material under investigation, with a small amount of Duco cement as binding material.

The essential result of this study is that cerium oxyfluoride CeOF exists as a stable compound. It has a face-centered cubic lattice of the CaF$_2$ type with a lattice constant which, depending on the amount of fluorine dissolved in the lattice, varies from 5.66 to 5.73 ± 0.01A, with reference to the CuK_α line 1.539A.

We succeeded in producing pure cerium oxyfluoride by baking mixtures of CeO$_2$ and CeF$_3$ in a small carbon arc furnace from 5 to 30 minutes at temperatures which are believed to be of the order of 3000°K. Quantitative transformation could be obtained if the mixture was chosen correctly. However, in agreement with Stintzing, we were not able to produce CeOF by oxidation of CeF$_3$. There is, consequently, a marked difference in the chemical behavior of the corresponding compounds of lanthanum and cerium. Whereas LaOF could be produced, by Stintzing, by oxidation of LaF$_3$, cerium oxyfluoride CeOF apparently can be produced only by reduction of CeO$_2$ with fluorine. Oxidation of CeF$_3$, on the other hand, always led directly to CeO$_2$ The influence of oxygen on the two oxyfluorides is very different also. Whereas baking at 1200°C for two hours in oxygen did not affect LaOF appreciably, temperatures above 300°C were sufficient for quantitative transformation of CeOF into CeO$_2$. To check this result in more detail, samples of CeOF were heated for one hour each at different temperatures in air. Whereas at 200°C only slight indications of CeO$_2$ lines could be found in addition to the strong CeOF lines, the strength of CeOF and CeO$_2$ lines was approximately the same after baking for one hour at 260°C. After baking at temperatures above 320°C, finally, only traces of CeOF lines were found besides the CeO$_2$ lines.

We appreciate greatly the help of Mr. S. M. Segal in the final experiments, particularly after one of us (A S.) had to give up the work prematurely.

[1] W Klemm and H A Klein, Zeits. f Anorg Chemie **248**, 167 (1941)

The Magnetic Susceptibility of Tungsten Bronzes

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STRAUMANIS et al.[1] have assumed that the yellow sodium tungsten bronzes of composition NaWO$_3$ contain tungsten in the pentavalent state and that the red, violet, and blue bronzes, which are deficient in sodium, correspond to solid solutions of WO$_3$ in NaWO$_3$ with varying ratio of W(V) to W(VI). We have determined the magnetic moment of several bronzes in order to cast more light on the probable oxidation state of tungsten in these systems.

Sodium and potassium tungsten bronzes were prepared by reduction with hydrogen of a molten mixture of tungstic oxide (WO$_3$) and the corresponding alkali metal tungstate (M$_2$WO$_4$). The composition of the sodium bronzes was determined by x-ray analysis as suggested by Straumanis;[1] that of the potassium bronze, by chemical analysis for potassium and for tungsten. Magnetic susceptibilities were measured by the Gouy method using an electromagnet at field strength 9000 gauss. The field strength was determined by calibration with standard nickelous chloride solution. The observed values for the susceptibility per gram atom of alkali metal are given in the first line of Table I.

In calculating the *theoretical susceptibility expected for a mixture of W(V) and W(VI)*, it is assumed that the orbital contribution to the magnetic moment is *not* quenched and, therefore, the "spin-only" treatment does not hold. Such non-perturbation of the multiplet structure seems to be fairly common with the heavier transition metals,[2] especially in octahedrally symmetrical crystalline fields such as obtain in these bronzes. Assuming Russell-Saunders coupling of the orbital and spin contributions, the expected moment for the W(V) ion is 1.55-bohr magnetons. The susceptibilities given in line 2 of Table I include corrections for the diamagnetic contribution of Na$^+$, K$^+$, O$^-$, W^{+6}, and excess WO$_3$. It is evident that the observed susceptibilities are considerably lower than those predicted on the assumption these bronzes contain pentavalent tungsten. Similarly, the observed susceptibilities are lower than *those predicted for a mixture of* W(IV) and W(VI).

The low magnetic susceptibility reported here together with the striking electrical properties described by Straumanis and Dravnieks[3] leads us to suggest that the alkali metal tungsten bronzes are actually solutions of the alkali metal in WO$_3$ with the alkali metal more or less completely dissociated into diamagnetic ions and free electrons. In such case, the magnetic behavior should

TABLE I Magnetic susceptibility of tungsten bronzes per gram atom of alkali metal

	Na$_{0.554}$WO$_3$ (21°C)	Na$_{0.956}$WO$_3$ (27°C)	K$_{0.53}$WO$_3$ (21°C)
Observed	5.8×10^{-6}	15.3×10^{-6}	194×10^{-6}
Calculated for W(V)	960×10^{-6}	940×10^{-6}	940×10^{-6}
Calculated for W(IV)	510×10^{-6}	510×10^{-6}	500×10^{-6}
Calculated for an electron gas	-10.9×10^{-6}	-5.8×10^{-6}	$-18.6 \times 10^{-}$

be predictable on the basis of an electron gas. Using Pauli's well-known equation[4] for the magnetic susceptibility of an electron gas and correcting for the Landau diamagnetism[6] we predict, after correcting for diamagnetic alkali metal ions and WO_3, the values given in line 4 of Table I for the magnetic susceptibility of the tungsten bronzes per gram atom of alkali metal.

The correspondence between the observed and calculated values is remarkably good, considering that even slight binding of the free electrons to the alkali metal ion introduces a paramagnetic correction to the values calculated on the basis of completely free electrons. The large disagreement, observed in the case of the potassium bronze, may be due to the greater polarizability of the potassium ion with consequent greater binding of the free electrons. The agreement in the case of the sodium bronzes is fully as good as that found for the pure alkali metals and better than that found for a saturated solution of sodium in liquid ammonia.[6]

Further work on these and other bronzes is in progress.

We are indebted to Dr. E. O. Brimm of Linde Air Products Company for sending us samples of the yellow and blue sodium bronzes. These bronzes were prepared by reduction with tungsten of a mixture of WO_3 and Na_2WO_4. Measurements on them are included in our results.

[1] M E Straumanis, J Am. Chem Soc. **71**, 679 (1949). This paper contains references to earlier work.
[2] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932), p. 312
[3] M. E. Straumanis and A Dravnieks, J. Am. Chem. Soc. **71**, 683 (1949).
[4] W. Pauli, Zeits. f. Physik **41**, 81 (1927).
[6] L Landau, Zeits. f. Physik **64**, 629 (1930).
[8] Yost and Russell, *Systematic Inorganic Chemistry* (Prentice-Hall, Inc., New York, 1946), p. 143.

Chemical Reactions in a Magnetic Field

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THE possible effects of applied magnetic fields on chemical reactions have been investigated in some detail[1,2] and in general it has been concluded that such effects, if they exist at all, are not great. Bhatnagar reported that the rates of certain inorganic reactions could be altered by approximately one percent by fields of the order of 10,000 gauss. However, Schmid, Muhr, and Marek[3] have reported that when styrene was polymerized at 80°C in a field of 16,000 gauss, an eightfold reduction in rate was observed. An explanation has been suggested for this phenomenon based on an orientation by the field of the spin moments of the unpaired electrons.[4]

The experiment reported above has been reinvestigated in this laboratory and the investigation has been extended to other reactions. An electromagnet was used which could provide a field of 14,000 gauss across a 1-in. pole space. The reactions in the field took place in a flat Pyrex cell under an inert atmosphere. This cell and a control removed from the field were maintained at a temperature of 80±0.3°C in a suitable thermostat. A field of 12,000 gauss was used for all experiments reported here.

Benzoyl peroxide is an effective catalyst for the polymerization of styrene and accordingly the effect of the field on the decomposition of this substance was investigated. Two grams of the peroxide were dissolved in 100 g of toluene and the reaction was followed until the peroxide was 70 percent decomposed. No measurable effect of the field could be observed, a result which

TABLE I. The polymerization of styrene in a magnetic field of 12,000 gauss.

Time (hr.)	Percent conversion in field	Percent conversion in control
1	11.2	11.4
2	19.9	20.0
3	28.1	28.2
4	35.7	35 9

agrees with that reported recently by Leffler[5] for a field of 7518 gauss. The catalyzed polymerization was then studied using 2.00 g of peroxide per liter of styrene. The results are given in Table I. The uncatalyzed polymerization of styrene was studied under the conditions described and also in a number of experiments in which carefully purified styrene was sealed in ampoules in the absence of air. In none of these experiments on the polymerization of styrene in a field of 12,000 gauss was any measurable effect of the field observed. A similar result has recently been reported by Breitenbach and Richter.[6]

The decomposition of hydrogen peroxide in a field of 12,000 gauss was also examined and no significant effect of the field on the rate of the reaction could be detected.

[1] Selwood, Chem. Rev. **38**, 41 (1946).
[2] Bhatnagar, Mathur, and Kapur, Phil. Mag. **78**, 457 (1929).
[3] Schmid, Muhr, and Marek, Zeits. f. Electrochemie **51**, 37 (1945).
[4] J. E. Leffler and M. J. Sienko, J. Chem Phys **17**, 215 (1949).
[5] J. E. Leffler, J. Chem. Phys. **17**, 741 (1949).
[6] Breitenbach and Richter, Monats f. Chem. **80**, 315 (1949)

The Barrier to Internal Rotation in Methylfluoroform

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SOME uncertainty exists in published values[1-4] for the barrier to internal rotation in methylfluoroform, CH_3-CF_3. We have re-examined its infra-red spectrum, particularly the critical long wave-length region to 300 cm^{-1}. Measurements were also made of the temperature dependence of several of the lower frequency bands as an aid in frequency assignment. Possible indirect values for the torsional frequency were obtained from combination and difference bands. The corresponding barriers were then compared with the statistical values for the barrier, computed from the fundamental frequencies in conjunction with recent structural data[5-7] and the calorimetric entropy.[1] Two internally consistent sets of frequency assignments are proposed. They lead to barriers of 1740, 2000 and 3210, 2800 cal./mole; the value 3000±200 cal./mole is considered more probable.

The spectrum of the gas was observed to 400 cm^{-1} with a Perkin-Elmer 12B spectrometer The KRS-5 region from 400 to 300 cm^{-1} was run on a similar instrument at M.I.T. through the courtesy of Dr. M. Kent Wilson of Harvard and Mr. R. S. McDonald of M.I.T. The sample of methylfluoroform was furnished by Dr. A. F. Benning, du Pont and Company. The spectrum observed agrees in most regards with that reported previously.[2] The temperature dependence of absorption listed in Table I was obtained in a sealed 7-cm gas cell[8] at a room-temperature pressure of 45 cm.

The various assignments of fundamentals are given in Table II and the Raman and infra-red spectra below 1200 cm^{-1} are given in detail in Table III. Concerning the A_1 assignments, the CH_3 bending, ν_2, is 1375^{-1} in ethane[6] and 1378 cm^{-1} in methylchloroform,[9] CH_3-CCl_3. Of the two bands, 1279 and 1410 cm^{-1}, nearest these values, 1410 cm^{-1} is most likely ν_2. This leaves the 1279

TABLE I. Temperature dependence† of some infra-red bands of CH_3-CF_3.

Band cm^{-1}	Percent transmission 20°C	Percent transmission 130°C	Percent transmission 190°C	Assignment
818	20	26	35	fundamental
829	12	13	17	fundamental
842	18	27	32	fundamental
910	62	46	32	difference band
1013	19	14	12	difference band
1090	40	30	19	difference band

† Qualitative observations of the weak 541 and 732 cm^{-1} bands revealed an increase in transmission over the same temperature range, indicating that they are not difference bands.