NEUTRON DIFFRACTION AND ITS APPLICATIONS IN INORGANIC CHEMISTRY

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I. Introduction

It is just 20 years since neutron diffraction was first used for studying solids and liquids. The fact that solids would diffract neutrons had been demonstrated in 1936 (*33*, *51*), but it was only with the advent of nuclear reactors that neutron beams became available with sufficient intensity to merit their use as a practical means of structural investigation. Since 1944 the intensity of the beams which can be obtained from reactors has increased by roughly two orders of magnitude, leading to corresponding improvements in the power of neutron diffraction techniques. The most important advances have been the increase in accuracy of the data which can be obtained, thus making the conclusions more informative, and the widening of the range of materials which can be studied, brought about by a reduction in the quantity of material needed for study. Twenty years ago, when neutron fluxes from reactors were no more than 10^{12} neutrons cm^{-2} sec^{-1}, powdered polycrystalline samples were almost always used. For most substances single crystals of sufficient size, roughly 1 cm in linear dimensions, were not obtainable, and even when the necessary size could be attained there were usually technical difficulties in interpreting the in-

tensities of the diffracted beams, because of the pronounced effects of secondary extinction. Now, as neutron fluxes in the range 10^{14} to 10^{15} promise to become available, the linear dimension of a suitable single crystal is reduced from 1 cm to 1 mm, leading to an enormous increase in the field of possible materials for study and a corresponding reduction in the difficulties of interpretation. The last few years have seen the steady appearance of automatic diffractometers (*22*, *24*) controlled by punched tape or similar device, which can be programmed to carry out a survey of reflections in three dimensions leading to a picture of the scattering density of the solid in three dimensions. Nevertheless, it must be remembered that even this crystal of much reduced size which now becomes adequate, or will soon be so, is considerably larger than is needed for X-ray diffraction observations. Many materials cannot be produced in large enough crystals; there remains therefore considerable restriction on the choice of material for examination, and there is no reason to suppose that these limitations will disappear within the foreseeable future. Quite apart from this, the main limitation on the rate of progress of neutron diffraction techniques, and on the rate of accumulation of information by using them, remains the fact that a nuclear reactor is needed as the primary neutron source. Over the past 10 years the number of suitable reactors has steadily increased and their geographical distribution has continuously widened. However, it is unlikely that there will be anything like such a general distribution of the "super reactor" of the 10^{14} to 10^{15} type, which will be needed to keep in the forefront of current research in this field. Therefore most of the progress will probably continue to be restricted to a few laboratories in the scientifically most advanced countries of the world.

The principles of neutron diffraction methods are now widely known and papers describing their use are distributed in a wide variety of journals, devoted mainly to physics, chemistry, and metallurgy, the fields in which the technique has been principally applied. A general description of the methods and their application to various fields of study has been given by Bacon (*10*), and more recently a broad account of their application to chemistry in particular has been published (*11*). The purpose of the present article is to survey the present position as it relates to inorganic chemistry, concentrating on accounts of investigations published within the last 3 or 4 years. In general therefore the reader should consult one of the earlier publications for an account of the principles of the subject and for details, with full reference to the original papers, of the earlier work. Here, as elementary introduction, we shall simply recall that, of the two basic applications of neutron diffraction, namely, the detection of "light" elements and the exploitation of the *magnetic* scattering of neutrons, it is the former that has been of most service to inorganic chemistry. We shall not deal

here with the determination of the magnetic structures of solids, i.e., their magnetic architecture, a problem of interest chiefly to physicists. We shall, however, discuss some observations of magnetic scattering in paramagnetic materials which have been used to deduce direct information about the valence states of certain atoms.

II. Heavy Element Compounds

The value of neutron diffraction for the determination of the structures of compounds of heavy elements arises because the scattering amplitudes of these elements are not very much larger than those of the light elements such as hydrogen, carbon, and nitrogen. This point will be clear from Table I, which lists the scattering amplitudes (or, more strictly, the scat-

TABLE I

SCATTERING AMPLITUDES b (IN UNITS OF 10^{-12} CM) FOR SOME ELEMENTS ARRANGED IN ORDER OF ATOMIC NUMBER

Element	Scattering amplitude	Element	Scattering amplitude	Element	Scattering amplitude
Hydrogen	−0.38	Calcium	0.49	Iodine	0.52
Deuterium	0.65	Titanium	−0.38	Xenon	0.48
Carbon	0.66	Vanadium	−0.05	Barium	0.52
Nitrogen	0.94	Chromium	0.35	Cerium	0.46
Oxygen	0.58	Iron	0.96	Holmium	0.85
Fluorine	0.55	Cobalt	0.25	Hafnium	0.88
Sodium	0.35	Nickel	1.03	Tungsten	0.47
Magnesium	0.53	Copper	0.79	Platinum	0.95
Aluminum	0.35	Bromine	0.67	Gold	0.76
Silicon	0.40	Zirconium	0.70	Mercury	1.31
Phosphorus	0.53	Niobium	0.69	Lead	0.96
Sulfur	0.31	Palladium	0.59	Thorium	1.01
Chlorine	0.99	Silver	0.61	Uranium	0.85
Potassium	0.35	Tellurium	0.56		

tering *lengths*) of a number of common elements and others which will be referred to in our later discussions. The elements are arranged in order of atomic numbers, but there is no very substantial increase of b as we go through the list. It will be realized, by comparison, that for the scattering of X-rays the amplitude with which any element scatters the radiation is proportional to its atomic number. As a result, the amplitude of the X-ray scattering by an atom, and even more the *intensity* of the scattering, is enormously greater for the heavy elements than for hydrogen, carbon, nitrogen, and oxygen. Another significant point of general interest to be noted from Table I is the fact that the scattering amplitude of deuterium

is considerably larger than that of ordinary hydrogen. There is therefore a marked advantage in preparing *deuterated* versions of materials to be studied with neutrons. Moreover, the benefit of the larger scattering amplitude is reinforced by the fact that deuterium, unlike ordinary hydrogen, does not give a large amount of *incoherent* scattering, which in the latter case produces an inconveniently large amount of background intensity in the diffraction patterns of polycrystalline or powdered samples.

A. Oxides and Related Compounds

Before the development of neutron diffraction there was no direct evidence for the structures of many of the simplest oxides of the heavy elements, and these had been inferred only indirectly from a knowledge of the unit cell and general spatial considerations. Attempts to study the uranium oxides with neutrons were made at an early stage, but only recently, as the greater neutron fluxes have permitted single crystals to be employed, have fully convincing and conclusive data been obtained. We may mention here another important advantage of using neutrons when accurate determinations of structure amplitude factors are required in chemical systems of this kind. Uranium, for example, has a very large absorption coefficient for X-rays, which means not only that observations are dependent on only a very thin surface layer of material, but also that it is very difficult to make precise allowance for the effect of absorption on the observed diffraction intensities. On the other hand, the absorption coefficient for neutrons is less by four *orders* of magnitude, thus leading to much more accurate and significant intensity data.

Willis (*69*), in particular, has studied the range of compositions in the uranium-oxygen phase diagram represented by UO_2, UO_{2+x}, and U_4O_9, the measurements having been made not only at room temperature but well beyond 1000°C. At room temperature it is found that the simple fluorite (CaF_2) model, in which the uranium atoms are placed at the corners and face-centers of the unit cell and the oxygen atoms are at the eightfold positions such as $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, gives an adequate description, and it is deduced that the thermal vibrations of both the uranium and oxygen atoms are isotropic. With increase of temperature, however, the vibrations of the oxygen atoms (but not the uranium) become strongly anisotropic, in such a way that there is greater motion along the four tetrahedral [111] directions. These are the directions in which the oxygen atoms move toward the holes which exist in the structure at points such as $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. The effect of this can be seen very directly in the neutron diffraction data by making a comparison of the variation with temperature for sets of reflections such as [755], [177], [933]. If the thermal motion was isotropic, then these reflections should all show the same temperature dependence, since they have

the same interplanar spacing, but, as Fig. 1 shows, they exhibit pronounced differences. In fact these results can be interpreted in two possible ways, either by assuming anisotropic motion across the $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ positions or by random displacements along the [111] directions toward the adjacent holes in the structure, but the second interpretation is considered to be unlikely. It is interesting to note that with calcium fluoride, CaF_2, itself there is

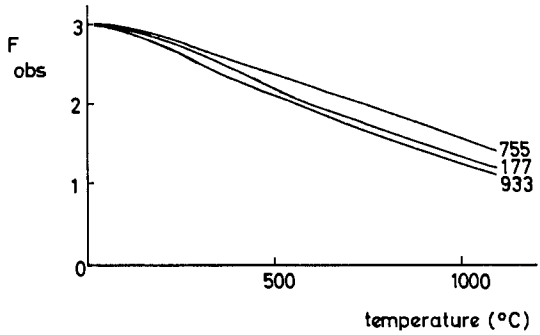

FIG. 1. The variation with temperature of the experimentally observed structure amplitude factors for the [755], [177], and [933] reflections of UO_2. From Willis (*69*).

evidence (*70*) for an asymmetry of vibration even at room temperature. When the neutron data are refined for fluorine positions specified as $\frac{1}{4} + \delta$, $\frac{1}{4} + \delta$, $\frac{1}{4} + \delta$, and the related positions, the conclusion reached is that δ has a finite value of 0.009.

When additional oxygen is incorporated, to yield the nonstoichiometric compounds UO_{2+x}, the observed variations of density suggest that the uranium lattice remains intact and the oxygen atoms go into interstitial positions. An examination of single crystals has shown that there is a marked increase in the angular range over which reflection of neutrons takes place, indicating considerable strain in the structure. At the same time the intensity variations show that extra oxygen atoms occupy positions that are distributed at random throughout the structure, so that, although the same space group symmetry $Fm3m$ is preserved, this now relates only to the "statistical" cell, obtained by superimposing all the cells in the structure. An important conclusion is that the randomly distributed "defects" are *not* individual oxygen atoms but complexes which consist of two vacant normal oxygen sites, two interstitial oxygens of type O′ and two interstitial oxygens of a second type, O″. These complexes are accordingly described as a "2:2:2 configuration." This complex is indicated in Fig. 2 in which the pairs of oxygens C,D and E,F replace the oxygen atoms which would normally be at A,B. As can be seen in this figure, the atoms C,D are dis-

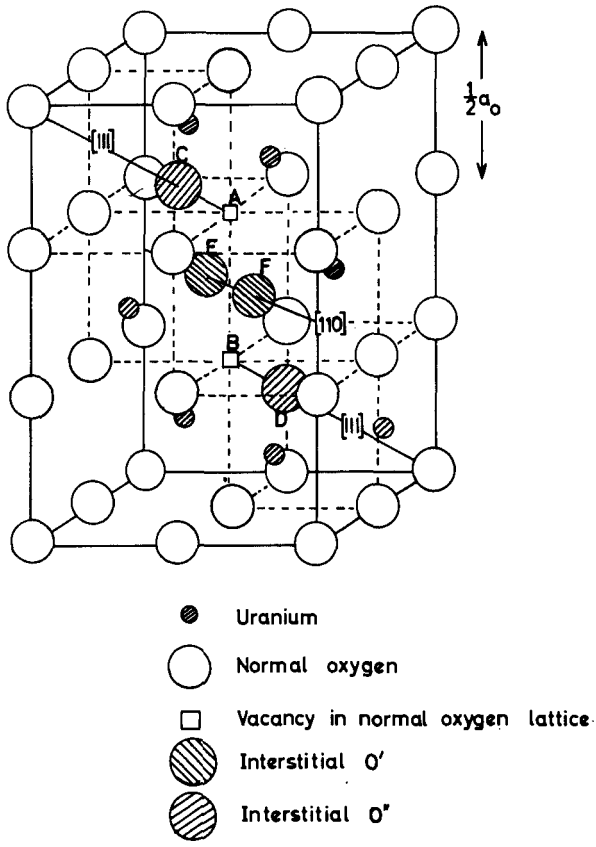

FIG. 2. A model of the UO_{2+x} structure showing the nature of the 2:2:2 complex. In UO_2 normal oxygen atoms would be present at A,B, whereas in UO_{2+x} they are replaced by a pair of oxygen atoms at C,D (displaced in the [111] direction) and a pair at E,F (displaced in the [110] direction). These two pairs, together with the vacant sites, constitute the 2:2:2 complex. After Willis (*69*).

placed about 1 Å in a [111] direction from a normal site, whereas the complementary pair E,F have moved about the same distance in a [110] direction.

When the value of x in the formula UO_{2+x} has increased to 0.25, i.e., at the composition U_4O_9, a new phase appears and it is known by X-ray studies (*15*) that long-range ordering occurs, with production of an enlarged unit cell, with a side of 4 times the original length and containing 64 of the original fluorite-type cells. The details of the oxygen positions in this supercell have not yet been fully worked out and will depend on a future refined interpretation of the superlattice reflections with neutrons.

However, from the neutron measurements so far (*69*), it has been established that the same kinds of 2:2:2 complexes occur as were shown to exist in UO_{2+x}. Thus it appears that the transition which occurs when the new phase appears at the composition U_4O_9 corresponds simply to an ordered linking together of these complexes.

Several studies have been made of the next phase in the uranium-oxygen system, namely, U_3O_8. Andresen (*5*) suggested a structure which was at variance with the conclusions of concurrent X-ray work by Chodura and Maly (*28*), which demanded a doubled unit cell. Loopstra (*48*) has repeated the neutron work under conditions which gave much improved angular resolution in the diffraction pattern and has confirmed Andresen's conclusions and his suggested structure. By trial-and-error methods, the structure was refined to a stage where the discrepancy factor had fallen to $4\frac{1}{4}\%$. Each uranium atom has seven oxygen neighbors and, for all the uranium atoms, six of these neighbors lie at distances between 2.07 and 2.23 Å. In addition, one of the three uranium atoms in U_3O_8 has a seventh oxygen neighbor at 2.44 Å, and the other two atoms have a seventh oxygen at 2.71 Å. This assignment of distances is therefore in agreement with the ionic states denoted by a formula $U^{6+}U_2^{5+}O_8$.

A series of heavy element oxides has been studied by Leciejewicz and his colleagues in Poland. In each case previous X-ray investigations had succeeded in conclusively placing the heavy atoms, but the positions of the oxygen atoms could only be inferred from spatial considerations. Only powdered materials were available for the neutron diffraction observations, but these proved to be sufficient to indicate the oxygen positions reasonably accurately. The orthorhombic form of lead monoxide, PbO, has been studied by both Leciejewicz (*46*) and Kay (*40*), and here it is found that the oxygen positions deduced after X-ray work (*25*, *26*) were wrong. It was found in fact that the oxygen atoms formed zigzag chains parallel to the *a* axis of the unit cell and that these, in turn, pack together to form layers of atoms parallel to the *ac* plane.

An investigation of the tetragonal form of tellurium oxide, TeO_2, by Leciejewicz (*45*) was related back to a very early X-ray study reported by Goldschmidt (*32*) in 1926, which postulated a rutile type of structure with space group $P4_2/mnm$. This had been subsequently discounted in 1948 by Stehlik and Balak (*63*), who had proposed a unit cell with a doubled *c* axis and a space group of either $P4_12_12$ or $P4_32_12$. The neutron results confirmed the doubled unit cell, $a = 4.80$ Å and $c = 7.63$ Å, but required considerable changes in the atomic coordinates which had been suggested for the oxygen atoms; this investigation provides a very good example of how quite simple neutron observations can often disprove earlier ideas. It will be noted from Table I that the neutron scattering amplitudes of tellurium and oxygen

are almost exactly equal. In fact the oxygen positions are so important in determining the intensities of the neutron reflections that the oxygen coordinates deduced from the X-ray work were found to give a discrepancy factor of 50%. By making a new choice of coordinates, this factor was reduced to 10%. The revised structure, illustrated in Fig. 3, is interesting

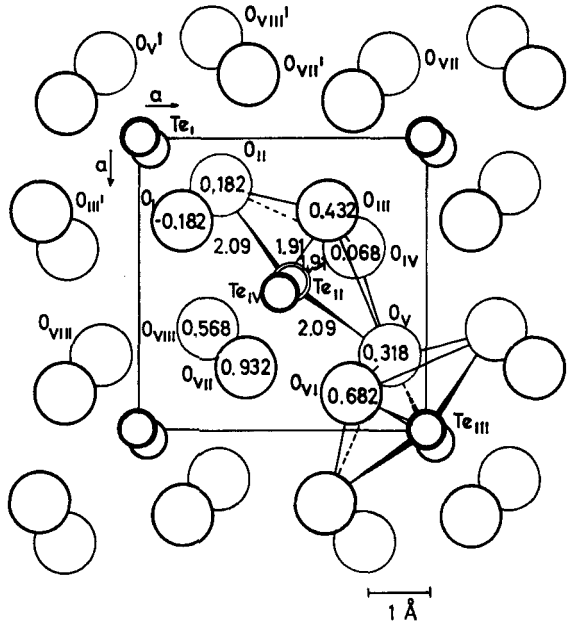

FIG. 3. The unit cell of tellurium oxide, TeO_2, projected on the [001] plane, indicating the two short tellurium-oxygen distances of 1.91 Å. After Leciejewicz (*45*).

because it requires two much shorter tellurium-oxygen distances of 1.91 Å, which suggest a type of predominantly covalent bonding.

By contrast, a simple rutile structure was found in PbO_2 (*47*) and all the diffraction lines could be indexed by assuming a unit cell for which $a = 4.95$ Å and $c = 3.38$ Å, with no evidence of a superstructure. As was mentioned, only the powder diffraction patterns of these simple structures were investigated; nevertheless, the single arbitrary parameter x which has to be determined, in order to fix the oxygen positions, can be decided quite accurately from a calculated plot of discrepancy factor R against x, based on the deduced model of the structure. Such a plot is shown in Fig. 4, from which it was concluded that $x = 0.309 \pm 0.004$. In fact Tolkachev (*65*) had suggested a value of 0.308 from his X-ray study, but without indicating the expected accuracy.

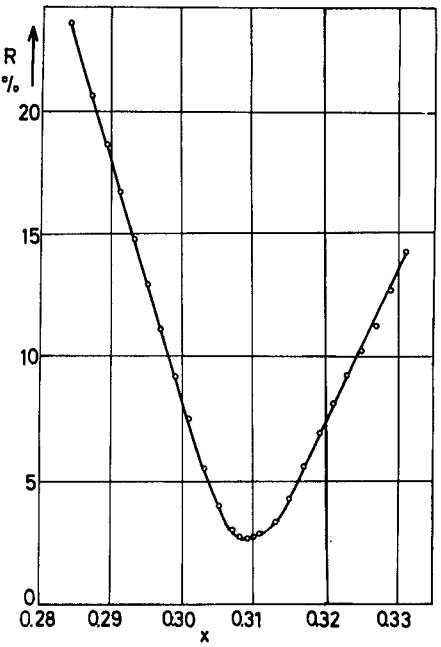

FIG. 4. Determination of the oxygen parameter x in PbO_2 by calculating the variation with x of the discrepancy factor, computed in terms of the deduced model of the structure. After Leciejewicz and Padlo (*47*).

Finally, to conclude our discussion of the location of oxygen atoms in the presence of heavy elements, we mention two studies from the recently installed neutron diffraction spectrometers at the nuclear research center in Puerto Rico by Almodovar *et al.* (*4*). A single-crystal analysis of the mineral scheelite, $CaWO_4$, has located the oxygen atoms to an accuracy of about 0.002 Å, showing the existence of a nearly regular WO_4^{2-} group with a tungsten-oxygen distance of 1.784 ± 0.003 Å. A study at the same reactor of $BaNiO_2$ has confirmed quite convincingly the rather surprising suggestion of Lander (*43*), from visually estimated X-ray intensities, that there was a square planar coordination of oxygen atoms by the nickel Ni^{2+} ions.

B. CARBIDES

A very extensive series of investigations of carbides, particularly the rare-earth dicarbides and sesquicarbides MC_2 and M_2C_3, has been carried out by Atoji and his co-workers (*6*, *7*). The dicarbides (*6*) have a simple tetragonal structure, shown in Fig. 5, for which the basic problem to be

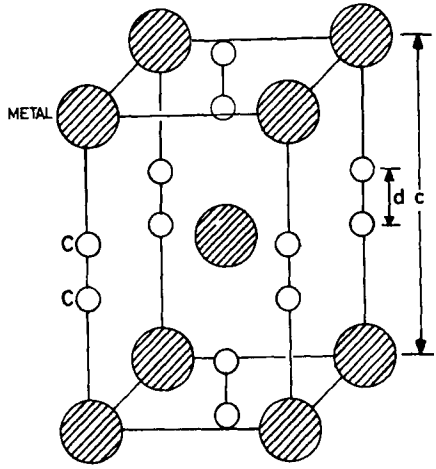

FIG. 5. The tetragonal structure of CaC_2 and the rare-earth dicarbides. The distance apart of the carbon atoms is represented by d.

solved by a neutron diffraction analysis is the determination of the carbon atom parameter which indicates the interatomic separation d of the two carbon atoms in the C—C group. This can be determined from observations with powdered materials in the manner discussed above for PbO_2. The experimentally determined structure amplitude factors are used to calculate the variation of discrepancy factor R for the assumed model as a function of the single parameter d. In this way Atoji has determined the C—C distance over a wide range of carbides. In CaC_2 it is found to be 1.19 Å, which is the same as for the triple bond in acetylene, but quite different from the 1.4 Å originally deduced from X-ray studies. On the other hand, in UC_2, which has metallic properties, the C—C distance is 1.34 Å which corresponds to a double bond. The rare-earth dicarbides offer an intermediate case with a separation which is practically constant at a value of 1.278 ± 0.002 Å. These conclusions may be summarized by writing the carbides of calcium, lanthanum, and uranium as $M^{2+}C_2$, $M^{3+}C_2$, and $M^{4+}C_2$ and stating that the C—C distance increases with the valency of the combined metal.

These determinations of atomic parameters have been followed by observations of the paramagnetic neutron scattering which have yielded direct conclusions about the magnetic moments, and hence the valence states, of the ions. Although the normal process of neutron scattering by atoms occurs because of an interaction between the neutron and the nucleus of an atom, nevertheless, there is an additional effect for the case of atoms which possess a resultant magnetic moment. This can be regarded

as an interaction between the magnetic moment of the neutron and the magnetic moments in the solid. In cases where there is cooperative magnetism, i.e., ferro-, antiferro-, or ferrimagnetism, then there will be additional neutron scattering into coherent Bragg peaks at sharply defined angles of scattering determined by the "magnetic unit-cell." From a study of these peaks it is possible to determine the "magnetic architecture" of the solid, namely, the quantitative details of the particular type of cooperative magnetism which exists. On the other hand, where there is only a random orientation of magnetic moments, in a paramagnetic material, then the portion of the neutron scattering which is magnetic in origin is broadly distributed over a wide angular range, as a general background to the neutron diffraction pattern. Measurements of this background have been used by Atoji to deduce the valency states of the metal ions in the carbides mentioned earlier. The procedure can be illustrated by the particular example of TbC_2, for which the experimental data are indicated in Fig. 6. The different

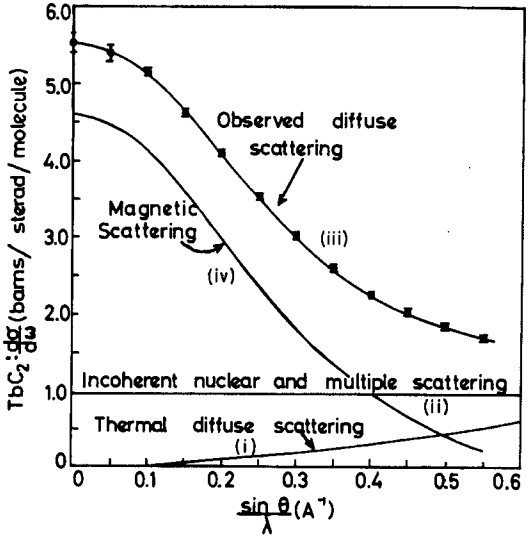

FIG. 6. Deduction of the magnetic scattering from TbC_2 by subtraction of the computed values of incoherent nuclear, thermal diffuse, and multiple scattering from the total experimentally observed diffuse scattering. After Atoji (*6*).

curves in the figure indicate the angular variation of the various contributions to the background. The components due to thermal scattering and incoherent nuclear scattering can be calculated and then subtracted from the total background which is observed experimentally, to yield curve (iv) in the figure, which represents, therefore, the contribution from the

randomly arranged magnetic moments. From the absolute value of curve (iv) when $\theta = 0°$ it is possible to calculate μ, the magnetic moment of the terbium ion, and this can then be compared with the calculated values for various possible valency states. The experimental value obtained for the scattering is 4.58 barns per terbium ion and this is in good agreement with calculation for an ion Tb^{3+}, for which the values of S, L, and J for the $4f$ electrons would be 3, 3, and 6, respectively, corresponding to the state $^7F_6$. A similar analysis carried out for cerium dicarbide established that the metal ions in CeC_2 were also in the trivalent state. In the case of YC_2, LaC_2, and LuC_2, it is the *absence* of paramagnetic scattering which establishes the trivalent nature of the ion. On the other hand, the observed scattering from YbC_2 led to the conclusion that only 83% of the ytterbium ions were trivalent and the remaining 17% were present as Yb^{2+}. Among the other carbides it was deduced, from the absence of magnetic scattering, that CaC_2 contained Ca^{2+} ions and, in the same way, the uranium ions in UC_2 were judged to be tetravalent. Further discussion of the bonding in the rare-earth compounds is expected, in the light of this demonstration that the ions are trivalent.

A series of rare-earth sesquicarbides La_2C_3, Ce_2C_3, Pr_2C_3, and Tb_2C_3 has been studied in a similar way by Atoji and Williams (*7*). These, too, have a sufficiently simple structure for it to be determined by powder diffraction methods, and the two positional parameters which need determination can be deduced from a least-squares analysis of the powder data. Except for the cerium compound, the C—C distance is found to be very close to 1.238 Å, which is significantly shorter than the 1.278 Å found in the rare-earth dicarbides discussed above, but appreciably longer than the 1.191 Å which occurs in CaC_2. The cerium sesquicarbide is different from the other sesquicarbides and shows an appreciably longer bond of 1.276 Å. This distinction is supported by the measurements of paramagnetic scattering which show that, whereas for La_2C_3, Pr_2C_3, and Tb_2C_3 the metal ions are entirely in the trivalent state, in the case of Ce_2C_3 about 35% of the cerium ions appear to be present as Ce^{4+}, which is a diamagnetic state.

C. Metal Hydrides

The metal-hydrogen system studied most fully is palladium-hydrogen, which was examined both for powdered materials by Worsham *et al.* (*72*) and for single crystals by Bergsma and Goedkoop (*16*). These studies showed that two phases can exist. At very low concentration of hydrogen only the α-phase is present, and it has a face-centered unit cell of 3.89 Å which is almost identical in size with that of pure palladium. It has not been found possible to ascribe any particular crystallographic positions to the few hydrogen atoms which can be taken up in this unit cell. With

increase of hydrogen content a β-phase appears which has a NaCl type of structure, but it is possible to fill only 70% of what we may describe as the "chlorine" positions in this cell. The hydrogen atoms which occupy these octahedral positions are distributed at *random* among them. Cable *et al.* (*27*) recently showed that nickel hydride behaves similarly. There are again two phases and in the β-phase it is concluded that the octahedral sites in this compound are about 60% filled. The hydride is unstable and decomposes into metallic nickel and hydrogen gas, with the result that the intensity of the reflection from the $NiH_{0.6}$ phase falls steadily during the measurements, with a corresponding increase in intensity of the nickel phase, as shown in Fig. 7, which indicates the time dependence of the

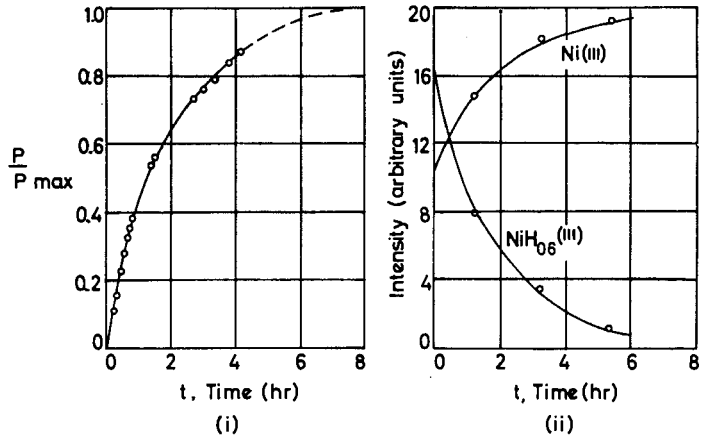

FIG. 7. The decomposition of nickel hydride is indicated by (i) the time dependence of the hydrogen pressure, and (ii) the simultaneous growth of the [111] reflection of nickel and decay of the [111] reflection of $NiH_{0.6}$. From Cable *et al.* (*27*).

hydrogen pressure and of the intensities of the two types of [111] reflection.

The hydrides of hafnium, zirconium, and titanium were studied earlier by Sidhu and his co-workers (*60*, *61*). In each case there is a single-phase hydride in which the hydrogen atoms can occupy, at random, most of the tetragonal holes in the ordinary face-centered unit cell of the metal. In this way the hydride approaches a fluorite type of structure at a composition MH_2. In the case of hafnium it is possible to reach a composition $HfH_{1.82}$ for this cubic structure, but further addition of hydrogen results in a transformation to a tetragonal form. With titanium, however, a much closer approach to the ideal composition can be achieved and it was found, for example, that $TiD_{1.971}$ (made with deuterium) was still cubic. The use of deuterium, rather than ordinary hydrogen, was fairly common in these

studies in order to avoid the high backgrounds in the powder diffraction patterns caused by the large incoherent scattering from ordinary hydrogen.

These investigations have been extended to the rare-earth metal hydrides by Cox *et al.* (*30*), who showed (as part of an investigation of the magnetic structures) that similar fluorite-type structures occurred for TbD_2 and HoD_2, and an earlier measurement by Holley *et al.* (*37*) had shown that the same arrangement existed for CeD_2. Indeed it had been shown that extra hydrogen could be taken up by CeD_2, and by the corresponding Pr and Nd compounds, in such a way that not only were all the tetrahedral sites occupied but there was a partial occupation of the octahedral sites as well. Further additional hydrogen can be taken up by the heavier rare-earth metals, such as Sm, Gd, Tb, Dy, Ho, Er, Tm, and Lu, which are known from X-ray diffraction data to form *hexagonal* trihydrides. The hydrogen positions in HoD_3, a typical example of one of these hexagonal structures which have the metal atoms in a close-packed arrangement, have been studied with neutrons by Mansmann and Wallace (*50*). The earlier X-ray work of Pebler and Wallace (*54*) had shown that the main difference between the unit cells of Ho and HoD_3 was an increased c axis in the latter case. This led to a suggestion that the hydrogen ions occurred in pairs of close neighbors parallel to the c axis and occupied all the tetrahedral and octahedral sites in the close-packed hexagonal metal matrix. It was found that the neutron diffraction pattern included superlattice lines which indicated the presence of a unit cell with a axes increased by a factor of $\sqrt{3}$, to give a unit cell three times the original volume and containing six units of HoD_3. Detailed examination of the observed intensities led to the conclusion that the hydrogen atoms are displaced from both the ideal tetrahedral and octahedral positions. The resulting structure, involving the determination of four positional parameters, provides nine nearest-neighbor hydrogen atoms for each holmium atom. Seven of these have interatomic separations lying between 2.10 and 2.29 Å and the remaining two are more remote, with a Ho—D distance of 2.48 Å. It is believed that the hexagonal trihydrides of the other rare-earth elements quoted above have the same type of structure as HoD_3.

A number of ternary hydrides have been reported and one of these, $AlTh_2D_4$, was examined with neutrons by Bergsma *et al.* (*17*), yielding a rather complicated structure which is not easy to interpret precisely from powder data. More recently Peterson *et al.* (*55*) have examined the rather simpler structure of $NiZrH_3$. This is an orthorhombic material in which the metal atoms are basically close-packed, with recognizable tetrahedral and octahedral holes, but there is considerable distortion from the ideal arrangement. One type of hydrogen atom is surrounded approximately tetrahedrally by a close zirconium neighbor at 1.96 Å, two more distant

zirconium atoms at 2.18 Å, and a nickel neighbor at 1.77 Å. On the other hand, the second type of hydrogen atom has five, rather than six, near-neighbors: there is a close zirconium neighbor at 1.95 Å, two others at 2.38 Å, and two nickel neighbors at 1.78 Å. No other metal atom is closer than 3.0 Å. These short Zr—H distances of 1.95 and 1.96 Å are definitely shorter than what would be expected, for example, by comparison with the distance of 2.09 Å found in ZrH_2 by Rundle *et al.* (*58*).

Finally, among the hydrides, we mention a study by Abrahams and Knox (*2*) of potassium rhenium hydride, a hexagonal compound which was reported by Ginsberg *et al.* (*31*) to have the composition K_2ReH_8. The conclusion from the neutron measurements, for which a single crystal was fortunately available, was that the hydride has the composition K_2ReH_9. No reasonable interpretation was found possible if only eight hydrogen atoms were included. Figure 8 shows the configuration deduced

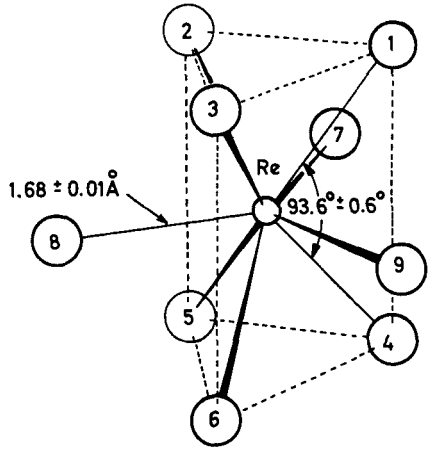

FIG. 8. The configuration of the $(ReH_9)^{2-}$ ion in potassium rhenium hydride, K_2ReH_9, deduced by Abrahams and Knox (*2*).

for the $(ReH_9)^{2-}$ ion. Six of the hydrogen atoms are located at the corners of a trigonal prism which has the rhenium atom at its center, and the remaining three are outside the centers of the prism faces; the average Re—H distance is 1.68 Å. The potassium ions have a configuration around the rhenium similar to that of the hydrogen atoms, but there is a much greater separation, 3.83 Å, between the rhenium and potassium atoms.

D. FLUORIDES

Neutron diffraction has made a useful contribution to the study of the recently discovered fluorides of xenon, and it is interesting to note that

XeF_2 and XeF_4 were among the first crystals for which three-dimensional intensity data were collected by Levy and his colleagues (*21*), using the automatic diffractometer at the Oak Ridge Laboratory. The particular contribution of the neutron studies was, as might be expected, to provide accurate measurements of the Xe—F separation. In the case of the tetragonal difluoride, for which 91 independent reflections were measured from a crystal measuring 1.5 × 1.0 × 0.5 mm and weighing only 2 mg, the Xe—F distance was found to be 1.984 ± 0.002 Å. This is the directly measured value of the interatomic distance and requires correction for the effects of thermal motion. The necessary correction is dependent on the nature of the relative motion between the two atoms. If it is assumed that the fluorine atom "rides" on the xenon atom, which is one of the modes of motion discussed by Busing and Levy (*23*) in their analysis of this correction, then the corrected value of the bond length is 2.00 ± 0.01 Å. It is the inaccuracy in specifying the type of motion which limits the accuracy of the determination of the bond length. In this compound, as can be seen in Fig. 9, the fluorine atoms lie vertically above and below the xenon atoms

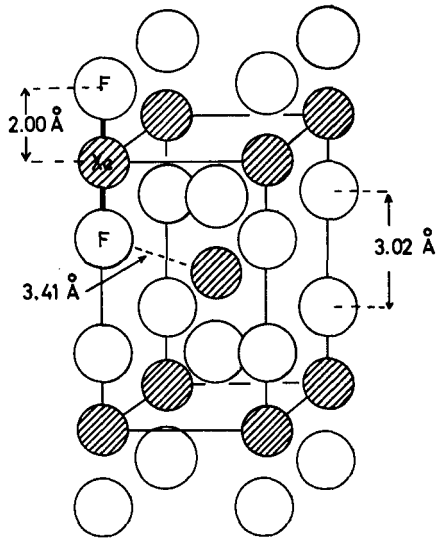

FIG. 9. The structure of xenon difluoride, XeF_2. Each xenon atom has two fluorine nearest-neighbors at a distance of 2.00 Å, and eight nonbonded neighbors at 3.41 Å.

and each of the latter has eight nonbonded neighbors at 3.41 Å. Each fluorine atom has one fluorine neighbor at 3.02 Å and four others at 3.09 Å.

For XeF_4 (*21*), which is monoclinic, a rather larger crystal weighing 25 mg was available and 623 independent reflections were measured. The

atomic coordinates deduced were in good agreement with those found from two independent X-ray determinations carried out at about the same time. In the case of the parameters which describe the thermal motion, however, the values obtained using neutrons were significantly higher than those measured with X-rays, and the reason for this discrepancy has not yet been found. The measured values of the two Xe—F bond lengths in XeF_4 are 1.932 and 1.939 ± 0.002, both of which yield a value within the range indicated by 1.95 ± 0.01 when they are corrected for thermal motion in a similar manner to that described for XeF_2. The structure is such that the XeF_4 molecule is planar. Each fluorine atom is separated by 2.74 Å from two fluorine neighbors which belong to its own molecule and is also in contact with eight atoms which belong to neighboring molecules and are at distances varying between 2.99 and 3.26 Å. The nonbonded contacts between xenon and fluorine atoms are at 3.25 and 3.22 Å. These observations with the xenon fluorides have resulted also in accurate knowledge of the neutron-scattering length for xenon—quoted as 0.476×10^{-12} cm.

A mixed fluoride also examined at Oak Ridge (*21*) is K_2NbF_7, for which a three-dimensional study has been made, using as a starting point the conclusions of a two-dimensional X-ray analysis carried out in 1939 by Hoard (*36*). The atomic coordinates were in good agreement with the earlier ones, but those determined with neutrons, as a result of measurements of 1358 independent reflections, were very much more accurate. In fact the standard deviations of the atomic positions were reduced to 0.001 Å for the niobium atom, and 0.002 Å for the potassium and fluorine atoms. The structure is of particular interest in respect to the detailed shape of the NbF_7 group. This is based on the addition of a seventh fluorine atom to a trigonal prism, having the niobium atom at its center, which would form an NbF_6 group. The extra fluorine atom is placed at the center of one of the square faces of this prism, but the ion is then distorted to such an extent that the Nb—F bond lengths all lie within the range 1.91–1.96 Å. The interatomic separations between the fluorine atoms vary much more widely, ranging from 2.36 to 2.91 Å.

Studies of uranium tetrafluoride, UF_4, have been reported on several occasions since Zachariasen's first description in 1949 (*73*) using X-rays. Kunitomi *et al.* (*42*) have carried out a further study of a polycrystalline sample using both X-rays and neutrons. Two methods of interpretation have been used, first, a trial-and-error adjustment of the fluorine coordinates in order to give good agreement between the observed and calculated neutron intensities and, second, the construction of radial distribution curves for the interatomic separation as revealed by X-rays and neutrons. The proposed structure is based on distorted UF_4 polyhedra with shared corners. A plan of the structure, but not the detailed coordinates, is given

in the original paper (*42*). Meanwhile an X-ray analysis of a single crystal, using molybdenum radiation and measuring 362 nonequivalent reflections, has been carried out by Larson *et al.* (*44*), who were able to deduce a full table of atomic coordinates and thermal parameters for both the uranium and fluorine atoms. The wide range of interatomic distances to which these coordinates lead emphasizes the difficulties involved in making a detailed deduction of the structure from the powder data.

III. Hydrogen Bonds

One of the earliest and most continuing applications of neutron diffraction to inorganic chemistry has been its use in establishing and detailing hydrogen bonds. This study has in fact related quite equally to both inorganic and organic chemistry, and several review articles have discussed the problem as a whole (*9*, *34*). Among the general problems which have been examined in some detail are (*i*) the nature of hydrogen bonds contributed to by the water molecules in hydrates and the geometry of these water molecules, (*ii*) studies of hydroxides, distinguishing between those like AlO(OH) which contain a hydrogen bond and others, such as $Ca(OH)_2$, which do not, and (*iii*) a study of the distinction which needs to be made between symmetrical and unsymmetrical bonds. A general survey of the earlier work on these topics is included in the writer's previous publication (*11*). Particular reference is now made, on the last of these three topics, to a recent article by Rundle (*57*).

A. $NaHF_2$ and KHF_2

Among the most interesting recent papers is an account by McGaw and Ibers (*49*) of their investigations of sodium hydrogen fluoride, in both the ordinary and deuterated forms, $NaHF_2$ and $NaDF_2$. Ibers (*39*) includes some related data for KHF_2. These authors emphasize the oft-repeated fact that it is not possible from diffraction observations, alone, to distinguish between a symmetrical hydrogen bond F—H—F in which there are anisotropic vibrations and one in which there is a random occupancy of two identical positions, one on each side of the midpoint of the bond. Least-squares analysis of their data shows that there is no significant change in agreement between the observed and calculated neutron diffraction intensities as the hydrogen or deuterium position is moved from the center by as much as 0.2 Å, so long as the amplitude of vibration is assumed to vary suitably. Figure 10 shows the correlations between vibration amplitude and choice of atomic position for the cases of both hydrogen and deuterium. The other parameters in the structure are very nearly independent of the position chosen for the H or D atoms and, in particular, the thermal motion deduced for the fluorine atom along the F—H—F bond

remains constant at a value of 0.015 Å for the mean-square amplitude. Since it seems very unlikely that the movement of the fluorine atom is larger than that of H or D, we can conclude from Fig. 10 that the deuterium

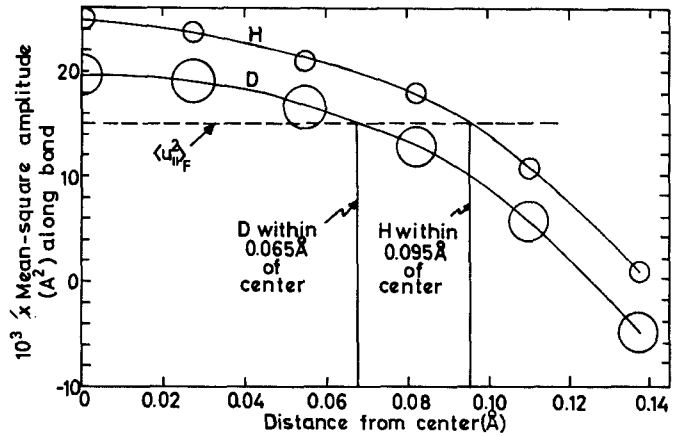

FIG. 10. Interpretation of the intensity data for $NaHF_2$ and $NaDF_2$ requires the correlation shown above between the mean-square amplitude of motion of H and D and the positions of H and D from the center of the bond. The motion of the fluorine atom along the bond is also shown, leading to the conclusion that the H and D positions must be within 0.095 and 0.065 Å, respectively, of the center of the bond. After McGraw and Ibers (*49*).

position is certainly within 0.065 Å of the center of the bond and the hydrogen position must be within 0.095 Å of it. If we accept that the difference between the motion of the hydrogen and fluorine atoms along the bond is due only to the stretching vibrations along this bond, then we can correlate the difference with the infrared data concerning these vibrations. McGraw and Ibers give the relation

$$(u_{\parallel}^2)_H - (u_{\parallel}^2)_F = (h/16\pi^2 m_F)\{[(2m_F - m_H)/m_H\nu_3] - 1/\nu_1\}$$

where u^2 and m represent mean-square amplitude and mass, respectively, and ν_1 and ν_3 are the symmetric and asymmetric stretching frequencies. The experimental values of ν_1, ν_3 are 600, 1577 cm^{-1} for $NaHF_2$ and 600, 1150 cm^{-1} for $NaDF_2$, leading to calculated values for $(u_{\parallel}^2)_H - (u_{\parallel}^2)_F$ of 0.0097 Å in $NaHF_2$ and 0.0062 Å in $NaDF_2$. Figure 11 shows these values in relation to the experimentally determined value of this expression, the latter being shown as a function of the assumed distance of the H and D atoms from the center of the bond. The figure, which includes an indication of the estimated accuracy of the data, provides very strong evidence that the F—H—F and F—D—F bonds in these compounds are symmetrical.

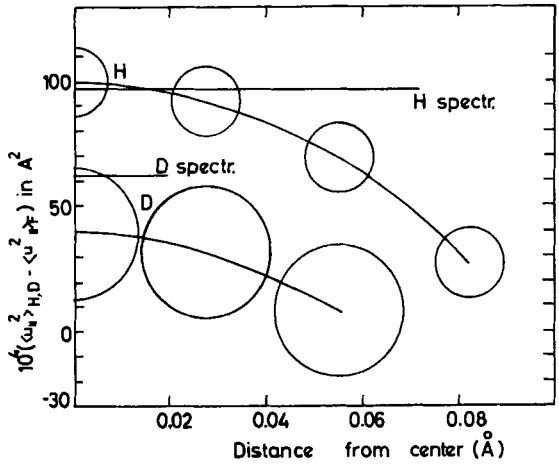

FIG. 11. The variation with atomic position, measured from the bond center, of the difference in mean-square displacement of the hydrogen and fluorine atoms in $NaHF_2$ and for deuterium and fluorine in $NaDF_2$. Only if the bond is centered are these values consistent with the deductions made from the frequencies of the infrared stretching vibrations along the bond. The circles represent the estimated standard deviations of the ordinate. From McGraw and Ibers (*49*).

As was mentioned, Ibers (*39*) has carried out a similar investigation with KHF_2 and, although the interpretation of the infrared spectrum is not so simple in this case, the same conclusion is reached in favor of a symmetrical bond.

B. HYDRATES

Among the recent studies of hydrates, that of $BaCl_2 \cdot 2H_2O$ by Padmanabhan *et al.* (*53*) was carried out to test the conclusions of a study of proton magnetic resonance by Silvidi and McGrath (*62*); these conclusions were not confirmed. In the structure deduced from a three-dimensional neutron analysis, measuring 1242 independent reflections, only three of the four hydrogen atoms in the formula unit are found to take part in hydrogen bonds to the chlorine ions. The fourth hydrogen atom appears to be loosely shared between two chlorine ions.

Baur (*14*) has examined the hydrate $MgSO_4 \cdot 4H_2O$ and finds that seven of the eight crystallographically different hydrogen atoms take part in hydrogen bonds between water molecules and oxygen atoms of the sulfate groups. The detailed conclusions reinforce the general conclusions arrived at from earlier studies of hydrates, such as $CuSO_4 \cdot 5H_2O$ (*13*). In particular, it is found that the water molecules themselves are very closely tetrahedral, with a mean H—O—H angle of 109.6°, whereas some of the O—O—O

angles are very different from this value, resulting in hydrogen bonds which are extremely bent. In fact, one of these bonds is bent by 40°, the largest value so far reported, which results in the hydrogen atom being 0.44 Å away from the straight line which joins the water and sulfate oxygen atoms. The mean O—H distance is 0.97 Å, the same as in copper sulfate, and the distances from hydrogen to the "acceptor oxygen" range from 1.82 to 2.06 Å, the latter being practically the same as the largest value found in copper sulfate. The general pattern of hydrogen atoms, showing the way in which these link together the oxygen atoms in the water molecules and sulfate groups, is illustrated in Fig. 12, which also indicates the unique

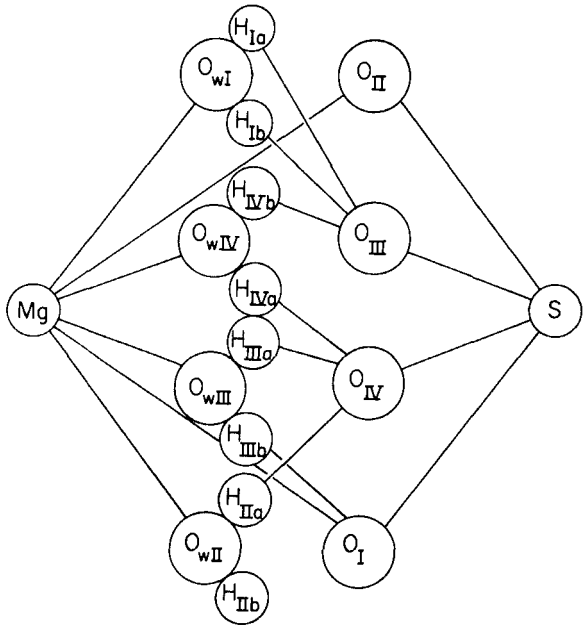

FIG. 12. The hydrogen-bonding scheme in $MgSO_4 \cdot 4H_2O$, indicating the unique nature of the eighth hydrogen atom, H_{IIb}, which is bonded only to the oxygen atom of its parent water molecule. Oxygen atoms such as O_{w1V} belong to water molecules; those such as O_{1V} belong to sulfate groups. After Baur (*14*).

nature of the eighth hydrogen atom, denoted by H_{IIb}. The only two oxygen atoms which could possibly be regarded as "acceptor" atoms for this atom are at distances of 2.39 and 2.59 Å, but these are far outside the range of O—H distance quoted above for hydrogen bonding. At the same time it is noteworthy that the thermal motion of this particular hydrogen atom is larger and more anisotropic than that of any of the others. There seems no

justification therefore for considering that it takes part in a hydrogen bond. A further example of very bent hydrogen bonds is provided by the water molecule in natrolite, one of the fibrous zeolites with the formula $Na_2Al_2Si_3O_{10}\cdot 2H_2O$, which has been examined by Torrie *et al.* (*66*). The water molecule is bonded to two oxygen atoms in the three-dimensional framework of oxygen tetrahedra. Both the bonds are long, being 2.84 Å and 3.00 Å, and it is not surprising to find that these weak bonds are very bent and that the water molecule succeeds in maintaining an O—H—O angle of 108°. The longer weaker bond is bent through the greater angle. A surprising feature of the results of this analysis is the low values found for the Debye thermal parameters. The authors suggest that the discrepancy may be due to errors caused by diffuse scattering, but it is not clear why their particular study should be distinctive in this respect.

Herpin and Meriel (*35*) have examined with neutrons a single crystal of potassium bicarbonate, $KHCO_3$, and their results are of particular interest when the hydrogen bond system is compared with that found in sodium bicarbonate and in sodium sesquicarbonate. In the case of $KHCO_3$ the main features of the structure can be seen in Fig. 13. There are asym-

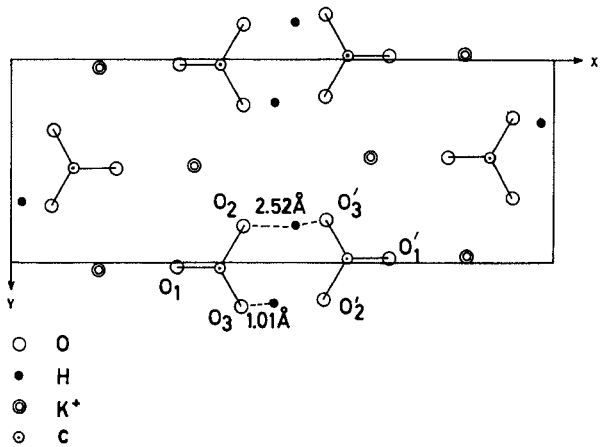

FIG. 13. A plan of the structure of potassium bicarbonate, showing the asymmetrical hydrogen bonds which link together pairs of carbonate groups. From Herpin and Meriel (*35*).

metrical hydrogen bonds linking together pairs of carbonate groups and it is concluded that the O—H distance is 1.01 Å, which is surprisingly short for the O—O distance of 2.52 Å, which represents quite a strong hydrogen bond. As the illustration shows, there are two hydrogen bonds between each pair of CO_3 groups, thus giving rise to a $(HCO_3)_2^{-2}$ group. This ar-

rangement is quite different from that which occurs in $NaHCO_3$, where there are infinite chains of $(HCO_3)_n$ ions, and is also different from that in the hydrated sodium sesquicarbonate (*12*), where $H(CO_3)_2^{-3}$ groups are joined by hydrogen bonds, provided by the water molecules, to produce chains of ions. The three different types of linkages in these compounds are contrasted in Fig. 14.

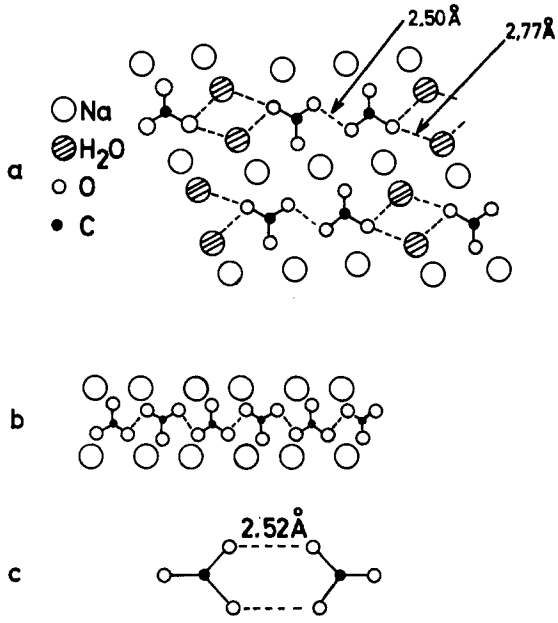

FIG. 14. A comparison of the hydrogen bonds in (*a*) sodium sesquicarbonate, $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, which contains a short bond of 2.50 Å, within an $H(CO_3)_2^{-3}$ ion, and two long asymmetrical bonds of length about 2.77 Å, (*b*) sodium bicarbonate, $NaHCO_3$, where there are infinite chains of $(HCO_3)_n$ ions, and (*c*) potassium bicarbonate, $KHCO_3$, where there are $(HCO_3)_2^{-2}$ ions. From Herpin and Meriel (*35*).

C. Other Hydrogen-containing Compounds

A study of a hydrogen oxysulfide, Ce_2OSH_2, has been carried out by the author and reported by Kramers and Smith (*41*). This compound may be regarded as derived from Ce_2O_2S, which was studied by Zachariasen (*74*), by replacement of one of the oxygen atoms by up to two atoms of hydrogen. The consequent change in size of the hexagonal unit cell is very small. In principle the hydrogen positions could be determined quite simply from a neutron study of single crystals. Unfortunately only powdered material was available, but some significant information was obtained from this, basically by a comparison of the diffraction patterns of the ordinary

and deuterated compounds. The two patterns are substantially different, because of the widely different scattering amplitudes of H and D, and lead to the conclusion that the hydrogen atoms do not occupy the positions vacated by the oxygen atoms, but distribute themselves among pairs of positions on the edges of the unit cell, midway between sulfur atoms.

Reference to a study of the hydrogen bonds in sucrose mentioned by Brown and Levy (*21*) is probably justifiable at this point, in spite of the fact that sucrose is not an inorganic compound. We mention it here because it is the most complicated structure that has been examined by neutrons so far and can therefore serve as the best example of the present power of the technique, so far as direct structural crystallography is concerned. The molecule, $C_{12}H_{22}O_{11}$, contains 45 atoms including 14 hydrogen atoms attached to carbon atoms and 8 others in hydroxyl groups. Using three different crystal specimens, weighing 80, 10, and 5 mg, respectively, the structure amplitude factors were determined for 2800 reflections. The discrepancy factor achieved by the analysis was 3.5% with standard deviations of 0.001–0.002 Å for the carbon and oxygen atoms, and 0.002–0.005 Å for the hydrogen atoms. Seven of the eight hydroxyl groups in the molecule take part in hydrogen bonds and two of these bonds are intramolecular.

IV. Miscellaneous Compounds

A. Solid Oxygen and Hydrogen

One of the less fundamental, but very practical, advantages of neutron diffraction techniques in comparison with X-ray measurements is the relative simplicity with which the intensity data can be obtained at low temperatures, and especially at 4°K using liquid helium. The advantage arises because the absorption coefficients of materials for neutrons are very much smaller than for X-rays, and there is no difficulty in constructing thin-walled metal cryostats, with radiation shields, through which both the incident and diffracted neutron beams may pass. Most of the applications which need low temperature measurement are investigations of magnetic properties, since in many cases it is only at very low temperatures that the magnetic forces, which give rise to cooperative magnetism between neighboring atoms, are sufficiently strong to overcome the disordering influence of thermal motion. Most of these studies are of physical, rather than chemical, interest.

From the point of view of the chemist, these low temperature techniques offer an opportunity of observing the reduction of thermal motion, and of studying in the solid form many of the simple molecules which are liquid or gaseous at ordinary room temperature. Solid oxygen and hydrogen have been examined in the U.S.S.R., to date only in the forms of poly-

crystalline material. The development of methods of growing and using single crystals at these temperatures would, of course, increase enormously the accuracy of the structural conclusions that could be obtained.

Ozerov *et al.* (*52*) have examined solid hydrogen and deuterium at 10°K. Both substances form crystals of tetragonal symmetry but they are not isomorphous, even though the two unit cells contain two molecules each and are of very nearly the same volume and exhibit closely similar nearest-neighbor distances. Detailed study of the reflections present reveals an unusual feature which seems to require the presence of more than one type of atom in each case and some degree of ordering between the two species. The investigators have suggested that there is ordering of the ortho and para molecules among the available sites, and that these two types of molecule have different coherent scattering amplitudes for neutrons.

In a later study of a rather similar kind, Alikhanov (*3*) recorded the powder diffraction patterns of solid oxygen at 27°, 20°, and 4°K. At the highest temperature the β-phase is present; on cooling there is an expected transition to an α-phase at about 24°K. Measurement at 27°K confirmed the existence of a rhombohedral unit cell, in agreement with previous X-ray measurements by Horl (*38*). There was some evidence of a magnetic contribution to the [111] and [110] reflections, but it has not yet been possible to interpret this in terms of any simple magnetic structure. Quite a different diffraction pattern is found at the two lower temperatures, and it is concluded that this pattern, at 20° and 4°K, represents the α-phase of solid oxygen. The pattern includes an additional low-angle line, which is believed to indicate that the α-phase is antiferromagnetic.

B. Spinels and Garnets

One of the earliest studies of an inorganic compound was an examination by the author (*8*) of magnesium aluminum spinel, $MgAl_2O_4$, to determine the distribution of the cations among the tetrahedral and octahedral sites which exist between the almost close-packed oxygen atoms. The conclusion reached was that the arrangement was "normal," i.e., that the magnesium atoms occupy the tetrahedral "A" sites and the aluminum atoms are in octahedral "B" sites, in contrast with the possible so-called "inverse" arrangement in which half of the aluminum atoms occupy "A" sites and the remaining Al and Mg atoms are distributed at random in the "B" sites. Stoll *et al.* (*64*) have made a further investigation to take advantage of the much increased accuracy which can now be achieved with a reactor possessing a higher neutron flux. They conclude that $MgAl_2O_4$ is not a completely "normal" structure but shows a degree of inversion between 10 and 15%. The precise amount of inversion is found to be dependent

on the thermal history of the sample. The value obtained for the oxygen parameter, which would be three-eighths in an ideal close-packed structure, is $u = 0.387 \pm 0.001$, the same value found in the earlier work. No significant effect of heat treatment on the value of u was found.

An interesting mineral compound examined at Grenoble (*29*) is the hydrogarnet $Al_2O_3 \cdot 3CaO \cdot 6H_2O$. The structure was found to be closely related to that of the garnet grossularite, $Al_2Ca_3(SiO_4)_3$. The nature of the similarity can be seen by writing the former formula as $Al_2Ca_3(H_4O_4)_3$, and the investigation shows indeed that a tetrahedron of hydrogen atoms replaces the silicon atom at the center of a tetrahedron of oxygen atoms. The arrangement is indicated in Fig. 15, showing the approximate tetra-

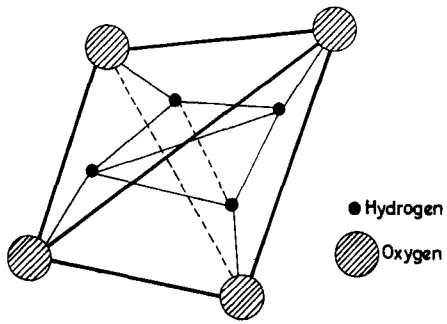

FIG. 15. The arrangement of an approximate tetrahedron of hydrogen atoms about the center of a tetrahedron of oxygen atoms in the hydrogarnet $Al_2Ca_3(H_4O_4)_3$. The four hydrogen atoms may be considered to replace the silicon atom in the garnet grossularite, $Al_2Ca_3(SiO_4)_3$. From Cohen-Addad *et al.* (*29*).

hedra of oxygen and hydrogen atoms which are centered on the same point. The oxygen tetrahedron has edges of 3.18 and 3.3 Å, appreciably longer than the edges of 2.8 Å found in the silicon garnet. The expansion may be considered to be due to the mutual electrostatic repulsion of the four H^+ ions which are largely contained within the oxygen tetrahedron. From the crystallographic point of view, the hydrogarnet therefore appears to be a hydroxide, $Al_2Ca_3(OH)_{12}$, but the oxygen-hydrogen distances, of which the shortest value is 1.13 ± 0.06 Å, seem to be significantly longer than for a normal hydroxyl group. Further study of a single crystal of the *silicon* compound has also been made, using neutrons, by Prandl (*56*), with the particular aim of achieving increased accuracy in locating the oxygen atoms. However, comparison with current X-ray observations (*1*) reveals unexplained discrepancies in the values of the thermal parameters of all the atoms.

V. Inelastic Scattering

In recent years the techniques of "inelastic" neutron scattering have been applied to the problem of determining the motion of ions and molecules in crystals. It can be shown very easily that the energy of a thermal neutron possessing a wavelength between one and a few Angstrom units is of the same order of magnitude as the energy of a single phonon of many of the vibrations which can occur in solids. This means that if a neutron gains or loses energy by exciting or de-exciting vibrations in a solid, then there will be significant changes in the energy of the neutron. It is possible therefore to determine some of the details of the spectrum of vibrations in the solid by studying the energy changes for neutrons.

Two experimental methods have been used so far. In the first, the neutrons have sufficient energy to excite vibrations and a determination is made of the *loss* of neutron energy. This method has been employed by Woods *et al.* (*71*) and Venkataraman *et al.* (*67*). In the second method, neutrons of much lower energy are employed, with an energy of about 0.005 ev which corresponds to a wavelength between 4 and 5 Å, and in this case the neutrons take up energy from the solid. Boutin *et al.* (*18*) have used the second technique in an examination of liquid and solid HF, KHF_2, KH_2F_3, and also for polyethylenes and a series of normal paraffin hydrocarbons. The experiment consists of observing the neutrons after they have been scattered through 90° by the sample under investigation. Their energies are measured by a chopper and time-of-flight technique so that it is possible to measure the increase of energy which has occurred during the scattering process. It must be realized, however, that not all vibrations will have an equal chance of being detected. In particular, because of the large scattering cross section of hydrogen relative to fluorine, the neutron data will exaggerate those motions in which movement of hydrogen atoms predominates. Moreover, it is the low frequency motions, with frequencies between, say, 30 and 1200 cm^{-1} and which give neutron energy gains between about 0.005 and 0.15 ev, that can be detected most readily. The information which is forthcoming can be illustrated by comparing curves for solid HF (at −120°C) and for KHF_2 (at 25°C) in Fig. 16. We draw particular attention to the sharp peak at an energy gain of 67 mv for HF and at 147 mv for KHF_2. This can be interpreted in terms of a motion of frequency ν in which the fluorine atoms move in phase with each other but out of phase with the intervening hydrogen atom. The value of ν will depend on the strength of the hydrogen bond and becomes progressively lower as the hydrogen bond becomes weaker, in agreement with the *increase* of the F—F bond length from 2.26 Å in KHF_2 to 2.49 Å in solid HF.

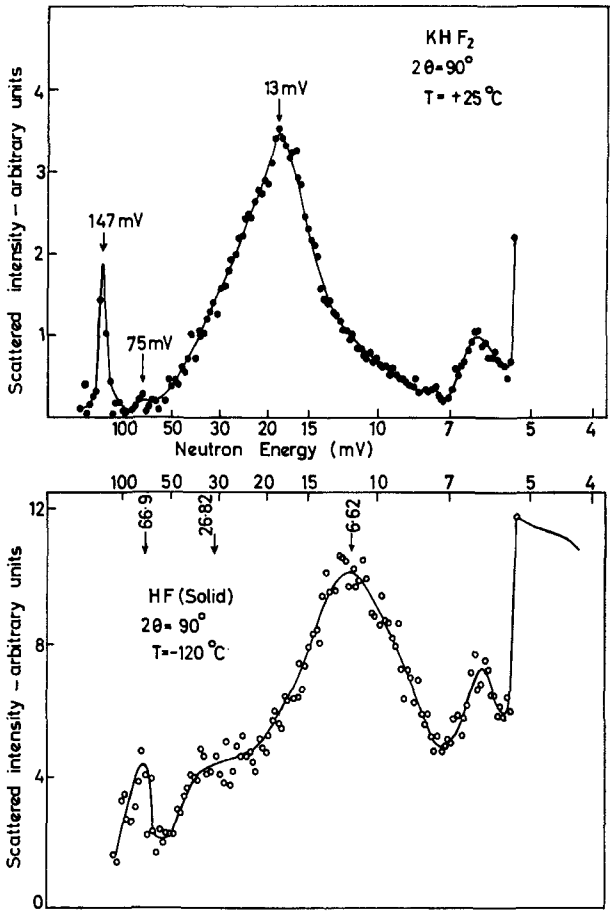

FIG. 16. A comparison of the spectra of inelastically scattered neutrons from solid HF and KHF_2, contrasting the high energy peaks which correspond to energy gains of 67 mv and 147 mv, respectively. The higher energy of the vibration in the latter case is a consequence of the shorter stronger hydrogen bond in KHF_2. From Boutin *et al.* (*18*).

This technique is now being applied to many other compounds. For example, some results have been given (*59*) for the alkaline earth hydroxides $Mg(OH)_2$ and $Ca(OH)_2$, and a preliminary account (*19*) has been given of a study of one of the hydrates, natrolite, mentioned earlier. It is reported that other hydrates are being investigated. It seems clear that the value of these studies will depend principally on the extent to which the energy distribution can be directly interpreted in practice.

A similar kind of investigation has been reported by Brajovic *et al.* (*20*), who examined the extent of rotational freedom which exists for the

NH_4^+ ion in several ammonium salts. In this case the variation of intensity of the scattered neutrons, as a function of the increase of energy which has occurred, is interpreted in terms of a calculation by Kreiger and Nelkin for the case of free rotation. The results are illustrated by Fig. 17, which

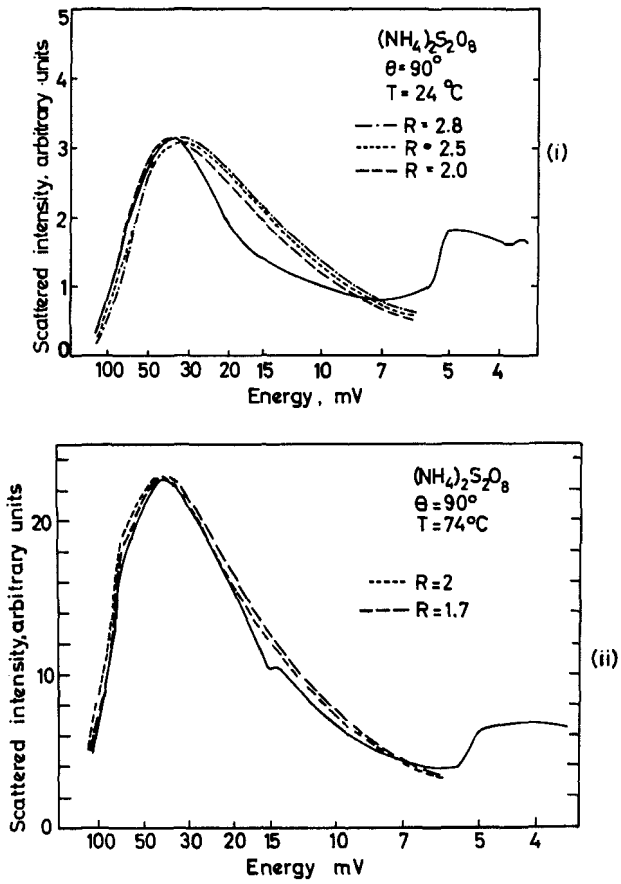

FIG. 17. A comparison of the spectra of inelastically scattered neutrons from $(NH_4)_2S_2O_8$ at (i) 24°C, and (ii) 74°C, in relation to calculated curves, with various effective rotational masses, on the assumption of free rotation of the ammonium ions. The results suggest that free rotation takes place at 74°C but not at 24°C. From Brajovic *et al.* (*20*).

compares the experimental data for $(NH_4)_2S_2O_8$, measured in turn at 24° and 74°C. At the higher temperature there is good agreement with calculation, if it is assumed that the "effective rotational mass" is equal to about twice the mass of a proton. At the lower temperature, on the other hand,

there is a marked difference from the calculated curves, whatever value be taken for the effective mass, and it is deduced that free rotation no longer occurs. In each case the increase in neutron intensity at the right of the curves, which rise to a maximum value at about 0.005 ev, is accounted for by considering those neutrons which have not undergone a change in energy. Rather similar conclusions are reached for $(NH_4)PF_6$, but in this case it appears that free rotation still occurs at 24°C but does not exist at −180°C. However, in spite of the satisfactory agreement between the observed and calculated curve shapes, the deduced values of the effective rotational masses are smaller than would be expected.

A recent study of torsional oscillations of the ammonium ion in NH_4Cl below room temperature, using the alternative technique in which the energy loss of higher energy neutrons is measured, has been made by Venkataraman *et al.* (*68*). The results are considerably more accurate than the earlier investigations (*67*), and the form of the spectrum of scattered neutrons and its variation with temperature suggest the existence of an anharmonic potential.

VI. Conclusion

We conclude this review by again emphasizing that the progress achieved in applying neutron-beam techniques to the study of both physical and chemical problems is linked very directly to the intensity of the neutron beams available. The *intensity* is the determining factor in two distinct ways. First, from the point of view of *inelastic* scattering, new techniques of analysis become available, and, second, considering conventional neutron crystallography, the accuracy with which both the atomic coordinates and the thermal parameters can be determined is considerably increased. Consequently, the strength and value of the chemical conclusions which can be reached are greatly magnified. We can perhaps sum up the present situation by quoting a remark made by Brown and Levy (*21*) in a discussion of their analysis of sucrose, "This determination must be considered at least as satisfactory as any X-ray determination done for a crystal of even approximately the same complexity." Bearing in mind also the problems, arising mainly in magnetic studies, which can be solved only with neutrons, this conclusion suggests that very substantial progress will continue to be made in the future.

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