Neutron Diffraction on HIFAR

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A brief account of the use of neutron diffraction as a complementary technique to X-ray diffraction in crystallographic analysis is given. The spectrometers to be installed on HIFAR are described and the experimental limitations of the technique discussed.

INTRODUCTION

Neutron diffraction has become an established technique for the study of solids but it will probably always remain a complementary technique to X-ray diffraction. In all investigations of atomic arrangement it is essential to obtain first all the information which can be obtained by X-ray methods.

This paper discusses the particular cases where neutron diffraction gives information unobtainable by X-rays and describes the neutron diffraction apparatus to be installed on HIFAR. No attempt is made to review the literature or to discuss the theory of neutron diffraction as these have been fully covered in a recent book (Bacon 1955) and in many publications, e.g., Wollan and Shull (1956), Bacon and Lonsdale (1953).

USES OF NEUTRON DIFFRACTION

In investigating the structure of solids by X-ray or neutron beams the angular positions and intensities of the diffracted spectra are determined experimentally and the atomic arrangements deduced from these measurements. The positions of the spectra are determined by the unit cell dimensions and their intensity by the positions of the atoms in the unit cell and by the manner in which the incident radiation interacts with the individual atoms. It is the process of scattering radiation by atoms which is very different for neutrons and X-rays and gives rise to the special uses of neutron diffraction.

X-rays are scattered by the electronic cloud around the nucleus while in most cases the neutrons are scattered by the nucleus alone. The important exception to this is the case of the magnetic ions which give additional scattering because of the interaction between their unbalanced electron spins and the spin of the neutron. This exception will be discussed later.

The atomic scattering factor for X-rays is markedly angularly dependent, falling off according to a form factor with increasing angle between the incident and scattered radiation. This occurs because the X-ray wavelength is about the same as the linear dimensions of the electron cloud with the result that radiation scattered from different parts of the atom is in phase only in the forward direction. The neutron wavelength, however, is very much greater than the linear dimensions of the nucleus so the nucleus may be regarded as a point scatterer and the neutrons are scattered isotropically.

The freedom of neutron diffraction from the necessity to make assumptions about the form factor gives it an advantage over X-ray diffraction in some applications particularly in investigtions of the degree of ordering in alloys and in the study of gases and liquids.

There are three main applications for which neutron diffraction has decided advantages.

Detection of light atoms in the presence of heavy atoms

The atomic scattering factor for X-rays increases regularly throughout the periodic table because of the continual increase in the number of extra-nuclear electrons. The ratio of the scattering factors for heavy atoms and light atoms is generally of the order of thirty or forty and since the diffracted intensity is roughly proportional to the square of the scattering factor, the observed spectra are very insensitive to the positions of the light atoms.

The scattering factor for neutrons, however, while it has a small steady increase due to increase in nuclear size, depends mainly on resonance effects which seem to vary in an arbitrary manner from atom to atom. As a result the neutron scattering factors for all atoms are roughly the same within a factor of 2 or 3 and the intensities of the diffraction spectra are sensitive to all the contributing atoms.

The heavy metal hydrides and carbides have been examined by neutrons and the positions of the light atoms, which cannot be located by X-rays, found. Studies of hydrogen bonds have been made in many substances, for example, sodium sesquicarbonate, α-resorcinol and benzene, using neutrons to locate the hydrogen atoms.

Differentiation between atoms of neighbouring atomic number

Because of the apparently random variation of neutron scattering factors with atomic number, ordering of alloys of elements close together in the periodic table can be detected. Thus ordering in alloys like FeCo and Mn_3Ni, undetectable by X-rays, can be easily found. However, ordering in Cu_3Au, which is easily shown by X-rays, cannot be found by neutrons since copper and gold happen to have identical scattering factors.

Magnetic Scattering

The interaction between the atomic magnetic moment and the spin of the neutrons provides the only direct method of determining the magnetic state of a material. In a

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paramagnetic material the atomic magnetic moments are randomly orientated and completely uncoupled so the magnetic scattering is completely incoherent and contributes only to the background.

However, in ferromagnetic, antiferromagnetic and ferrimagnetic substances coherence appears between amplitudes scattered from the ordered magnetic moments giving rise to diffraction peaks.

If the magnetic unit cell is the same size as the structure unit cell the magnetic diffraction peaks will coincide with the nuclear peaks and the total intensity will be the sum of the nuclear and magnetic intensities. In some substances the magnetic cell has twice the dimensions of the nuclear cell and the magnetic reflections occur at superlattice positions. This occurs, for example, in the antiferromagnetic oxides MnO, NiO and CoO.

The magnetic intensities depend on the orientation of the magnetic moments relative to the incident and scattered beams so it is possible in principle to determine the orientations of the magnetic moments relative to the crystallographic axes. In practice this determination is complicated by domain effects.

Since the interaction is between the electron and the neutron there is a magnetic form factor expressing the fall off in magnetic scattering factor with angle. However, unlike the X-ray case where the form factor is due to all the electrons in the atom, the magnetic form factor comes only from the electrons which contribute to the atomic magnetic moment. Therefore the magnetic form factor can be inverted to give the radial distribution of the magnetic electrons in the atom.

LIMITATIONS OF NEUTRON DIFFRACTION

The limitations on neutron diffraction arise almost completely from the relatively low fluxes available. Similar difficulties do not occur in X-ray diffraction since the number of quanta per unit area in a normal X-ray beam is greater than that in a neutron beam by a factor of 10^5. A compromise has always to be made between an incident beam intense enough to give observable diffraction spectra and resolution good enough to prevent considerable overlapping of the spectra.

Some of the more serious limitations are listed below. The numerical values given apply to reactors with a maximum thermal flux of 10^{12} neutrons cm^{-2} $sec.^{-1}$.

An attempt is made to assess the improvement which will be gained by using HIFAR where the thermal flux in the holes used for neutron diffraction is 7×10^{13} neutrons cm^{-2} $sec.^{-1}$.

Specimen Size

It is not possible to use very small crystals. Single crystals must be of the order of 2 by 2 x 5 mm. and powder specimens of about 7 cc. On HIFAR it is hoped to reduce the size of single specimens to $\frac{3}{4} \times \frac{3}{4} \times 2$ mm.

Resolution

Because of the low flux the monochromatisation cannot be very strict. At present specimens of lower symmetry than tetragonal cannot be examined as powders because of overlapping of the lines. Again it is hoped that the higher intensity from HIFAR will make more rigorous collimation possible and resolution equal to that of X-ray methods obtainable.

Experimental methods

Neutron diffraction data are much more laborious to collect than X-ray data. Photographic techniques are at present unsatisfactory and all information must be collected by counters. The weight of the counter and shielding ($\sim$ 2 cwt.) means that the counter must be restricted to movement in the horizontal plane. This restricts examination to one layer line unless the crystal can be adjusted to bring each layer in turn into the plane of the counter.

Because only one reflection can be examined at a time the collection of single crystal data is a laborious process. A reasonable estimate of the time taken is one hour for each reflection. It is unlikely that this time will be reduced.

The counter covers the same region in one traverse as an X-ray powder pattern but since the diffracted spectrum is only detected while the counter passes through the Debye-Scherrer ring only a small fraction of the diffracted neutrons are recorded. To compensate for this long exposure times are necessary. The average time is about 12 hours and in many cases it is necessary to average over several patterns.

Background intensity

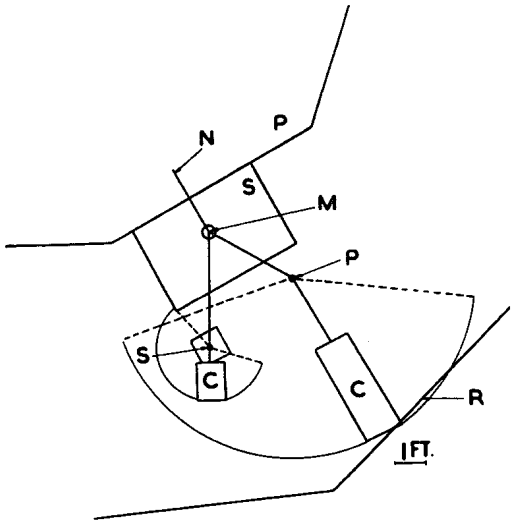
When a crystal contains an element having nuclear spin or a mixture of isotopes then there is a different scattering cross-section for each spin state and for each isotope. This mixture of scattering cross-sections gives rise to a high incoherent background which can be very troublesome. The incoherent scattering is particularly high in hydrogenous materials and in many cases single crystal methods must be used or the hydrogen replaced by deuterium.

FACILITIES ON HIFAR

Thermal neutrons from a pile have a Maxwellian energy distribution with the peak at approximately 1.5A°. The experimental arrangement for neutron diffraction consists of a collimator to extract a parallel beam from the pile, a monochromator to select a beam of monochromatic neutrons and a spectrometer carrying the specimen and counter.

The collimator size is chosen to give the best compromise between intensity and resolution. It is essentially a steel tube 5 feet long with a cross-section of about 2 by 1 inches. With these collimator dimensions the angular spread in the incident beam is about $\frac{3}{8}$°.

The monochromator consists of a large single crystal orientated so that the wavelength reflected is near the peak of the distribution curve. The crystals used are copper, lead and calcium fluoride, giving wavelengths of 0.81A°, 1.09A°



N	NEUTRON BEAM
P	PILE
S	SHIELDING
M	MONOCHROMATING CRYSTAL
P	POWDER SPECIMEN
S	SINGLE CRYSTAL SPECIMEN
C	COUNTER
R	RAILING ON FUEL ELEMENT STORAGE BLOCK

FIGURE 1: Plan view of spectrometers installed on pile face.

and 1.20A° respectively. Wavelengths on the short wavelength side of the peak are chosen to keep the second order contamination in the monochromatic beam to a minimum. In practice the second order component is about 2 per cent.

Two spectrometers will be installed on HIFAR. The first is a powder spectrometer. To obtain adequate resolution and low background the specimen-to-counter distance must be large and the counter well shielded. The specimen-to-counter distance is about 5 feet and the background should be about 30 counts per minute. This instrument cannot be used for single crystal work.

The second spectrometer is a single crystal instrument with a two to one ratio between counter rotation and crystal rotation. Since the counting rates for single crystals are much higher than for powders and the line width is governed by the specimen and not by the resolution of the instrument, a much smaller counter can be used and a specimen-to-counter distance of about 6 inches.

The method of recording the data will depend on the steadiness of the flux from HIFAR. Two methods can be used.

(i) The neutron pulses from the counter can be fed through a ratemeter on to a pen recorder and a continuous chart record obtained.

(ii) The counter can be moved a set angular interval when a certain number of counts have accumulated in a monitor placed in the beam from the monochromator. The number of counts received by the counter during this interval can be printed on tape.

The high penetrating power of neutrons makes neutron diffraction at high and low temperatures a simple matter, since reasonably thick furnaces and dewar flasks are transparent to neutrons.

The layout of apparatus at the pile face is shown in Figure I.

The whole apparatus must be adequately shielded to prevent unwanted neutrons entering the counter and to enable the operator to remain at the pile face for long periods without danger. On HIFAR the radiation level in the working area will be 1 maximum permissible level.

CONCLUSION

The instruments described in this paper will be operating early in 1959. Initial work will be single crystal studies of the antiferromagnetic oxides NiO and CoO and powder studies of ceramic systems, but spectrometer time will be available for other problems.

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