ROLE OF NEUTRON BEAMS IN UNDERSTANDING THE STRUCTURE OF ALLOYS, FERROELECTRICS AND SEMI-CONDUCTORS

by

V. V. Agashe

Naval Chemical and Metallurgical Laboratory, Bombay

ABSTRACT

Our knowledge of materials is advanced to a great extent with the help of optical, X-ray and electron beams, yet certain problems like order/disorder in alloys of metals having neighbouring atomic numbers, magnetic moment of magnetic alloys and compounds, position of atoms/ions in ferroelectrics cannot be solved with these techniques alone. Fortunately neutron beams, because of their interaction with nuclei, can give us a detailed information about these problems. This paper reviews the experimental technique of neutron diffraction. Certain problems in alloy constitution, ferro-electricity and magnetic moments are discussed in light of the information obtained from neutron diffraction studies.

Introduction

The microscope is limited by one important factor namely its resolving power. This is dependent upon the wavelength of the light used for making the observation. This limitation can be somewhat improved by using ultra-violet light ($\simeq 3 \times 10^{-5}$ cm.) or phase contrast microscopy.

Structures larger than 10^{-4} cm. become visible under the microscope in polished and etched specimens. In the size range 10^{-4} to 10^{-6} cm. X-ray methods have been useful in the study of the mechanism of age hardening, the coercive force in magnets and the problems connected with resistance to deformation. In the 10^{-7} cm. range the segregation, which leads to one type of age hardening, occurs. Finally and most important of all, X-rays can be used to investigate structures on the scale of 10^{-8} cm. This is the order of magnitude of the unit atomic pattern in the crystalline structure of alloy phases. In addition to the older substitutional and interstitial types of solid solutions, new type of defect lattice has been discovered in which there is a large percentage of empty places which would normally be occupied by atoms of parent lattice.

However an X-ray diffraction photograph merely indicates the co-existence of two phases but reveals nothing about the form of the aggregation. There are also many examples of poly-phase systems of finely crystalline products formed by mutual transformations and phase transitions in metallic systems, wherein morphological investigations are necessary. These studies

have to be done by using a beam of electron waves. By using suitable magnetic/electric fields for lenses and electron beam for light beam, one can construct a microscope having much higher resolving power. This is the principle of a modern electron microscope. The electron waves are also being used in many investigations of surface structure. When structure and nature of very thin films are to be determined, X-ray diffraction is unsuitable as X-rays pass through it very easily. The electron waves, as they cannot penetrate much thickness of matter can be used with advantage. Electrons accelerated through a potential of 30 KV will have approximately a mean free path of only about 400 Å in a metal. This would be the thickness to which electrons can penetrate roughly while retaining their power to form an interference pattern. The surface phenomena like oxidation, corrosion, nature of polish layer (Bilby layer) and lubrication can be studied with electron diffraction.

X-rays and electron waves (to a certain extent) interact only with the electron cloud of the atom and hence the scattering amplitude (of X-rays or electron waves) depends upon the atomic number. It is, therefore, not possible by normal methods of X-rays to distinguish between neighbouring elements such as iron and cobalt, when they occur together in a compound. Similarly it would be very difficult to distinguish between the different isotopic atoms in a crystal, (the electron cloud would be the same and hence X-ray scattering). In cold worked metals X-ray lines are broadened. There are two reasons for this broadening, lattice distortion and particle size. With the help of X-rays it is very difficult to pin one of the two reasons in a sample under consideration. In a few cases one can get success only after applying detailed Fourier analysis.

In certain ferroelectrics ($BaTiO_3$, KH_2OP_4) the properties of a domain are changed by applying a field. From other properties like specific heat, magnetic susceptibility, electrical conductivity one can infer certain ionic-atomic displacements in the crystal. However, X-rays have been unable to show it. In a magnetic alloy, the total magnetic moment depends upon the way in which the constituents are distributed and also on the orientation of individual atoms. Though from variation in sp. heat and magnetic susceptibility with temperature one can infer the distribution of the position of individual atoms to a certain extent, a complete and true crystalline picture of these alloys is not possible.

It can be seen very easily that most of the problems referred above depend for their solution on the state of the nucleus of the atom. They could be solved if we use a technique which will use the interaction with the nucleus and not alone with electron cloud of atoms (as in X-rays). Fortunately neutrons interact with matter in two ways. One is the short range interaction of the neutron with the atomic nucleus and the other which is only important for magnetic systems involves the interaction of magnetic moment of neutron with atomic moments. Neutron has no charge and has spin $\frac{1}{2}$. Its mass is 1838·6 times electron mass.

Elasser[1] suggested that the neutrons could be diffracted by crystalline matter. By using neutrons from a radium-beryllium source, Hallan and Preiswerk and Mitchell and Powers demonstrated neutron diffraction experimentally in the same year. However neutron diffraction as a practical research tool could only be possible after beginning of atomic age. Nuclear

reactors can give the high thermal neutron fluxes which are necessary for successful application of neutron diffraction.

If we consider neutrons which have made a large number of collisions with atoms in an atomic pile at temperature T before being allowed to escape from the pile, then they will have a root mean square velocity v appropriate to that temperature given by $\frac{1}{2} mv^2 = \frac{3}{2} kT$, when k is Boltzman Constant. According to De Broglie, a particle having a velocity v will have a wave length given by $\lambda = h/mv$. By substituting proper values in these equations, we find that the wave-lengths corresponding to root mean square velocities of neutrons in equilibrium at temperatures of O°C and 100°C are 1·55 Å and 1·33 Å respectively. It is most fortunate that these wave-lengths are just the magnitude desired for the investigations of atomic arrangements, since it will be neutrons having temperature of this order which can be conveniently obtained from an atomic pile. By inserting a collimator into the pile face, a beam of neutrons can be extracted. The neutrons in the beam will have a Maxwellian distribution of velocities. Assuming that the neutrons in the pile are in equilibrium at temperature T the nature of the wave-length distribution in such a collimated beam can be determined[2]. If ν_λ is the number of neutrons emerging per second with wavelengths between λ and $\lambda + d\lambda$ then

$$\nu\lambda = \frac{2N_1}{\lambda}\left(\frac{E}{kT}\right)^2 e^{-E/kT}$$

where N_1 is total number of neutrons of all velocities emerging per second.
E is the energy of a neutron of wave length λ.

The curve in Fig. 1 shows the variation in the number of neutrons counted per minute in the beam diffracted by a single crystal of calcium fluoride set successively to reflect various wavelengths*. It is clear from the curve (Fig. 1) that the spectrum is white resembling a beam of white X-rays without the supposition of any characteristic radiation. From white neutron beam we can get a monochromatic beam by keeping a single crystal with interplaner spacing 'd' making an angle θ given by '$\lambda = 2d \sin \theta$' coincides with A in Fig. 1.

Experimental layout of a neutron spectrometer

Similar to X-rays, neutron beams can be used for crystalline investigations as monochromatic or as white beams. In the case of X-rays the radiation comprises solely of a single line or a close doublet of the X-ray spectrum (for example, CuKα line). The monochromator separates this line from the general wave lengths which constitute the background of white radiation. In neutron case there is no equivalent of the line spectrum and the monochromator merely selects a band of wave-lengths. The width of this band is determined largely by the angle of divergence in the horizontal plane of the incident beam from the

*This curve will not be exactly identical with the distribution of wavelengths in the incident beam since the variation of the reflectivity of calcium fluoride crystal with wave length will have to be taken into account.

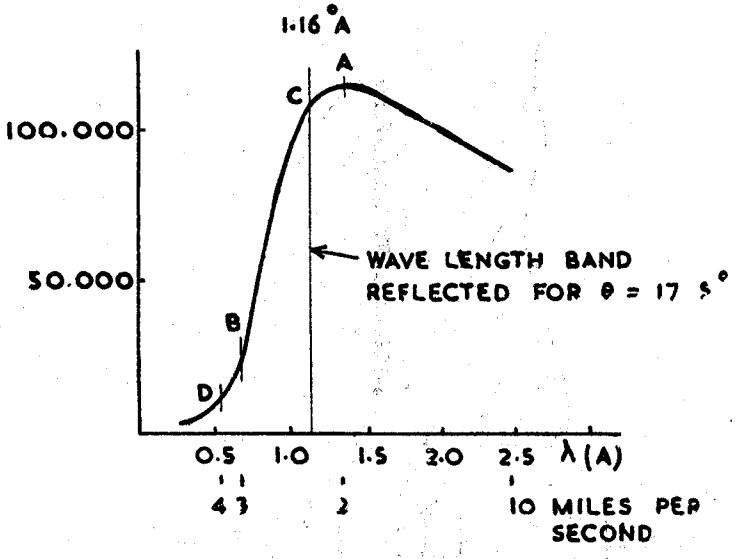

FIG. 1—Counting rate of collimated beam when reflected by calcium fluoride crystal.

collimator. In practice, this angle has sufficient number of neutrons in the beam to give adequate counting rates. This results the wavelength band to be of the order of 0·05 Å in width.

A neutron spectrometer (really a diffractometer) essentially consists of a collimator, a monochromator, a rotating table to mount the diffracting sample and a counter (Fig. 2). Arrangements for the rotation of the diffraction sample and the counter are necessary. In constructing a neutron spectrometer, the most important thing to be considered, is shielding from neutrons scattered by air molecules and by solid matter in their path. The shielding is essential for protecting both the operator and the detecting apparatus (the counter) from the main beam of neutrons and γ radiation which emerges from collimator. Only one percent of neutron beam from collimator is reflected by a monochromator and subsequently used in neutron diffraction measurements. The remaining neutrons will undergo scattering. The scattering is harmful to the personnel and also it will give a large background in measuring instrument. The scattering is reduced as far as possible by surrounding the monochromator, specimen table, and the counter with several inches of borated paraffin (Fig. 2). The paraffin serves to slow down such neutrons as are above thermal velocities, thus assuring that practically all the neutrons will subsequently be absorbed by the boron, the atter has a very high absorption coefficient for slow neutrons.

The collimator which is inserted through a hole in the pile face, is usually made of steel and is about 5 ft. in length and 5 inches in diameter. The aperture near the pile face measures about $1\frac{1}{2}$ inch vertically and $1\frac{1}{8}$ inch horizontally. The aperture on the other side of the collimator is such that the horizontal divergence of the beam is not more than about 3°/8. This divergent beam is reflected by a monochromator. The beam is then subsequently defined by cadmium slits A and B and is then available for diffraction of the specimen.

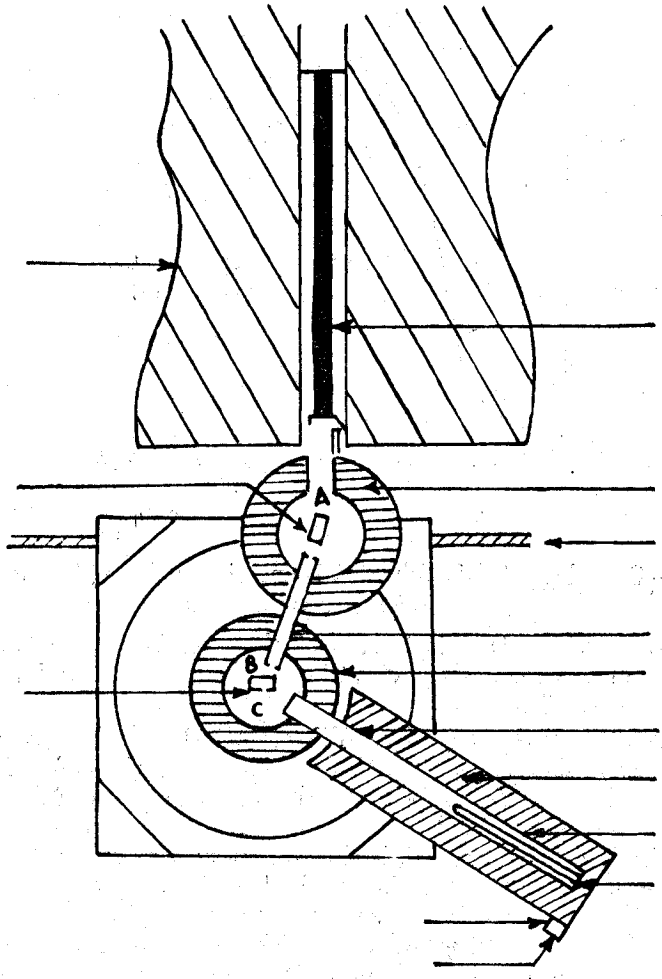

FIG. 2—Experimental layout of the neutron spectrometer (at Harwell).

The purpose of the monochromator is to select a narrow band of wave-length from the white neutron spectrum. A certain number of neutrons (having a wave-length λ) from the neutron beam incident on the crystal at an angle θ will be reflected by Bragg's eqn. $\lambda = 2d \sin \theta$. At first sight, it would appear that the angle (θ) chosen should be such that the wave-length (given by $\lambda = 2d \sin \theta$) coincides with the peak of the curve (Fig. 1). The presence of second order reflections, however, modifies this conclusion, for example, the calcium fluoride crystal cut with (111) plane parallel to the surface, when oriented to give 1·5 Å beam, would also give contribution from (222) reflection ($\lambda = 0{\cdot}75$ Å). It is preferable, therefore, to choose a wave-length such as C on the short wave-length side of the peak, whose second order (D) would be below the counting rate of the counter.

In the earliest experiments, metallic halide crystals particularly LiF, NaCl, and CaF_2 with mosaic spreads were used. (Wollan and Shull[3]). Sturm[4] has shown that the reflectivity increases when LiF surface is roughened.

LiF, further, has relatively high absorption ($\mu = 4\ cm^{-1}$) so that penetration is small. Later Shull and Wollan[5] showed that the metallic crystals (copper, lead) gave intensities two or three times greater than that of LiF and therefore are now in general use. These crystals can be used in 'transmission' or 'reflection'. Copper and lead have cut off wave-lengths round about 5 Å. McReynolds[6] has shown that the crystals of magnetite or germanium both of which have large cut off wave-lengths (9 Å) and weak second order reflections can be used with advantage for producing long wavelengths.

The form and size of diffracting specimen depend considerably on the particular problem under consideration. In the case of a powder, it should be packed in a thin container of a metal such as aluminium, which has low neutron absorption. If the specimen is in the form of a single crystal it can be directly mounted on the table. The metal container or the single crystal must uniformly be bathed in the neutron beam.

The neutrons diffracted by the specimen are received in a counter which can be rotated about the centre of the spectrometer. The counter is a proportional counter filled with boron trifluoride enriched in boron isotope of mass 10. (Fowler and Tunnicliffe[7]). To obtain adequate counting efficiency (about 80 per cent) the counter has to be about 2 ft. in length and 2 inches in diameter. A counter of this size surrounded with sufficient shielding material weighs about 200 lbs. (A conventional spectrometer weighs about 3 tons). Due to its heavy weight, the counter in operation has to be rotated automatically by means of an electric motor. The counter impulses after amplification and passage through a discriminating circuit (which rejects small pulses due to γ radiation) may be fed to the scaling units. It is found in practice that the recording of the diffraction pattern has to be done very slowly. The slow rate of recording is necessary because of the weakness of the diffracted peaks and appreciable background intensity. At any point counting has to be carried out for a sufficient length of time so that the statistical fluctuations in the rate of arrival of neutrons at the counter will, of course, give a counting rate enormously greater than that of from an equal volume of powder. In its reflecting position (in a single crystal) the whole of the reflected neutrons will enter the counter whereas a powder sends its diffracted radiation into conical haloes and only about 1 per cent of it is detected. Fig. 3 shows comparison of single crystal and powder diffraction of potassium bromide at $\lambda = 1{\cdot}08$ A (Backon, page 78). In practice, however, the majority of the structural investigation made so far by neutron diffraction have used the powder method, as the difficulties from secondary extinction are avoided.

Wollan, Shull and Marney[8] have reported the equivalent of an X-ray Laue photograph with photographic recording. A collimator beam about 0·5 sq. cm. passes through a crystal plate placed at the collimator aperture and diffracted beams are detected by an X-ray film, which is covered by an indium foil. The blackening of a photographic film is caused by the β particles which are produced by neutron capture in the indium foil. The X-ray film is quite insensitive to neutrons in absence of the activated foil. Laue patterns have been published for a number of substances like quartz, LiF, calcite; $NaNO_3$. Exposure of about 10 hours is required for crystals a few mm. thick.

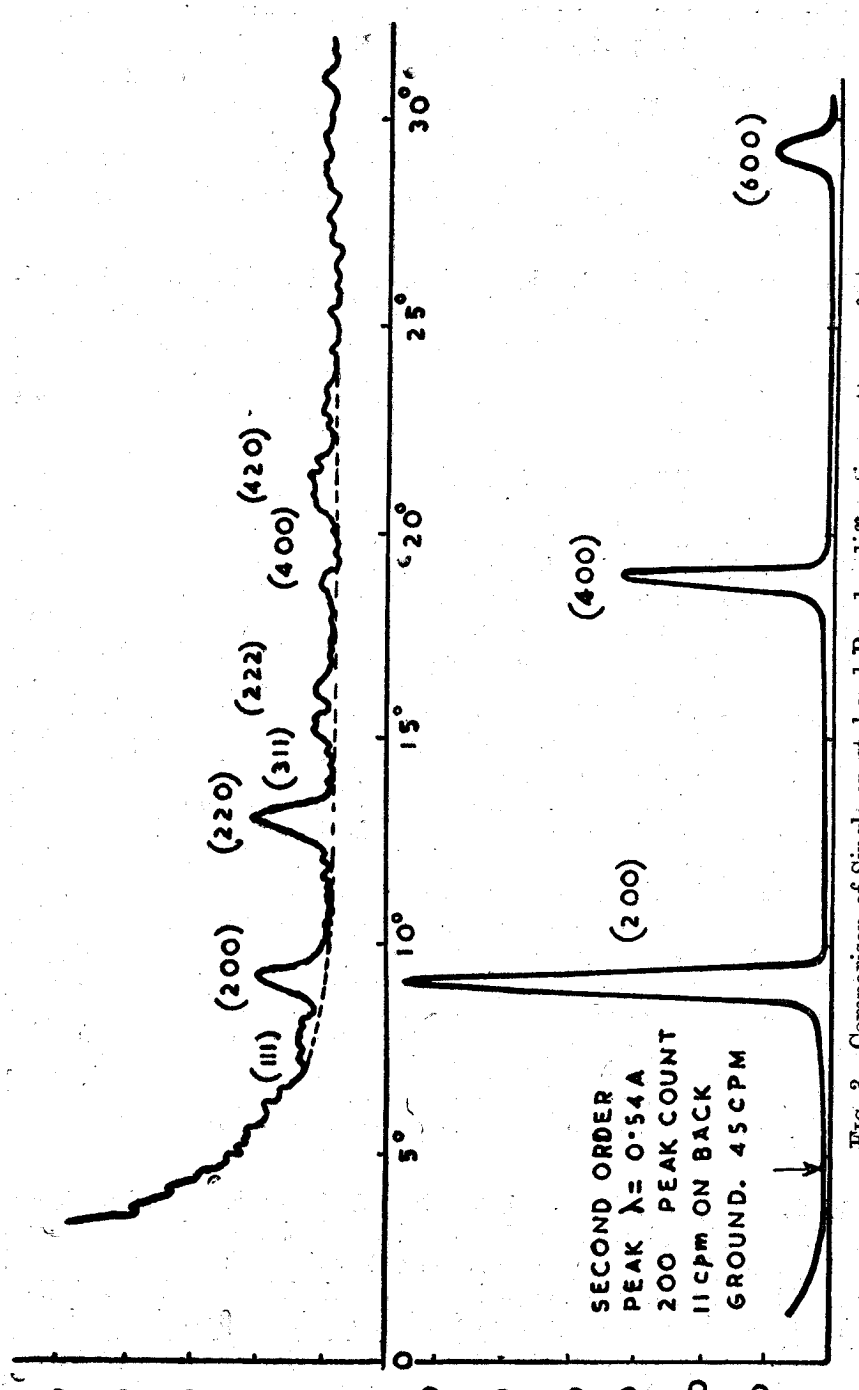

FIG. 3—Comparison of Single crystal and Powder diffraction patterns of potassium bromide ($\lambda = 1{\cdot}08$ A).

Applications

The interpretation of diffraction patterns in terms of atomic arrangement depends upon sign and magnitudes of scattering amplitudes of the elements. The scattering amplitudes ($\overline{b}$) can be known by (*a*) determination of refractive index (for sign of amplitude), (*b*) measurement of cross section by transmission experiments and (*c*) measurement of intensities of coherent Bragg peaks in diffraction patterns. All these values for the elements and for most of their isotopes today are known mainly due to three research groups, Oak Ridge National Research Laboratory, U.S.A.; Atomic Research Establishment Harvell, U.K. and Chalk River Project, Canada. This knowledge has somewhat made future work and interpretation easier.

Alloys

Many alloy systems contain constitutional solid solutions in which the constituents are distributed at random among the available atomic sites in the structure. In certain systems, suitable thermal treatment may cause the development of 'super lattice' in which the two types of atoms take an ordered arrangement with respect to each other, e.g. in the case of a b.c.c. structure, A atoms (one constituent) will be at cube corners, while B atoms (other constituent) at the body centre. This would be the ordered phase. In the disordered phase the atoms A and B will be distributed at random. The structure factor for (100) reflection will be $b_1 - b_2$ where b_1 and b_2 are structure factors for corner and centre positions. In the case of random arrangement $b_1 = b_2 = \frac{1}{2}\chi$ $(b_A + b_B)$ where b_A and b_B are corresponding values of A and B constituents, and the intensity of (100) reflection is zero. For the ordered arrangement the structure factor $(b_A - b_B)$ will have a finite value (unless $b_A = b_B$). Thus the appearance of order will produce extra lines in diffraction pattern. This phenomena is well known in FeAl, or Cu_3Au X-ray diffraction. But now consider alloys like FeCo, Ni_3Mn, CuZn. It would be seen from Table (1) that scattering factors for X-rays are very nearly equal (as the number of electrons in these elements is very nearly equal), and hence $(b_A - b_B)$ will be very small quantity, and superlattice lines will be very weak. However, it can be seen that neutron scattering factors for the same elements are quite different, and $(b_A - b_B)$ will have a finite value. This will give enough intensity for superlattice lines and thus decide whether or not the alloy is ordered. Fig (4) shows the diffracted peaks of Ni_3Mn and FeCO. The intensities of superlattice lines are enhanced on account of negative scattering amplitude of Mn. Certain alloy systems also could be studied by suitable choice of isotopes for their individual constituents. An alloy of $MnNi^{60}$ will have weak normal diffraction lines and intense superlattice lines, since normal manganese and Ni^{60} have amplitudes of neutron scattering practically equal in magnitude but of opposite sign (Table 1). The scattering of neutrons can differ markedly from one isotope to another. The neutron which has a spin $\frac{1}{2}$ can interact with a nucleus having a spin i. With these spins either parallel $(i + \frac{1}{2})$ or anti-parallel $(i - \frac{1}{2})$, the scattering amplitudes associated with these two interactions can be widely different in magnitude and may also differ in sign.

TABLE 1*

X-ray and neutron scattering amplitudes

Atom	fx for X-rays at Sin θ/λ = 0·5 Å	Neutrons b
Al	1·55 × 10^{-12} Cm.	0·35 × 10^{-12} cm.
Fe	3·3	0·96
CO	3·4	0·28
Au	12·3	0·76
Cu	3·8	0·76
Zn	3·9	0·59
Mn	3·1	—0·37
Ni	3·6	1·03
Ni^{58}	3·6	1·44
Ni^{60}	3·6	0·30
Ni^{62}	3·6	—0·87
O	0·62	0·58
Mg	1·35	0·54
Ge	4·2	0·84
As	4·4	0·63
Si	1·72	0·40
P	1·83	0·50

* These values are taken from Bacon-neutron diffraction, page 28.

Spinel Structures

Many metal oxides of the type XY_2O_4 have spinel structure. This consists of a close packed arrangement of oxygen ions with two types of interstices for the cations. In the unit cell which contains eight molecules, there are so called A sites which are tetrahedrally co-ordinated by oxygen atoms and 16 B sites which are octahedrally co-ordinated. In 'normal' structure X occupies A sites and Y, B sites. In 'inverse' structure, A sites are occupied by eight Y atoms and B sites are occupied by X atoms and remaining eight Y atoms. Verwey and Heilman[9] have pointed out that normal and inverse arrangements are the only two extremes of a continuous range of cationic distribution which satisfy the spinel structure.

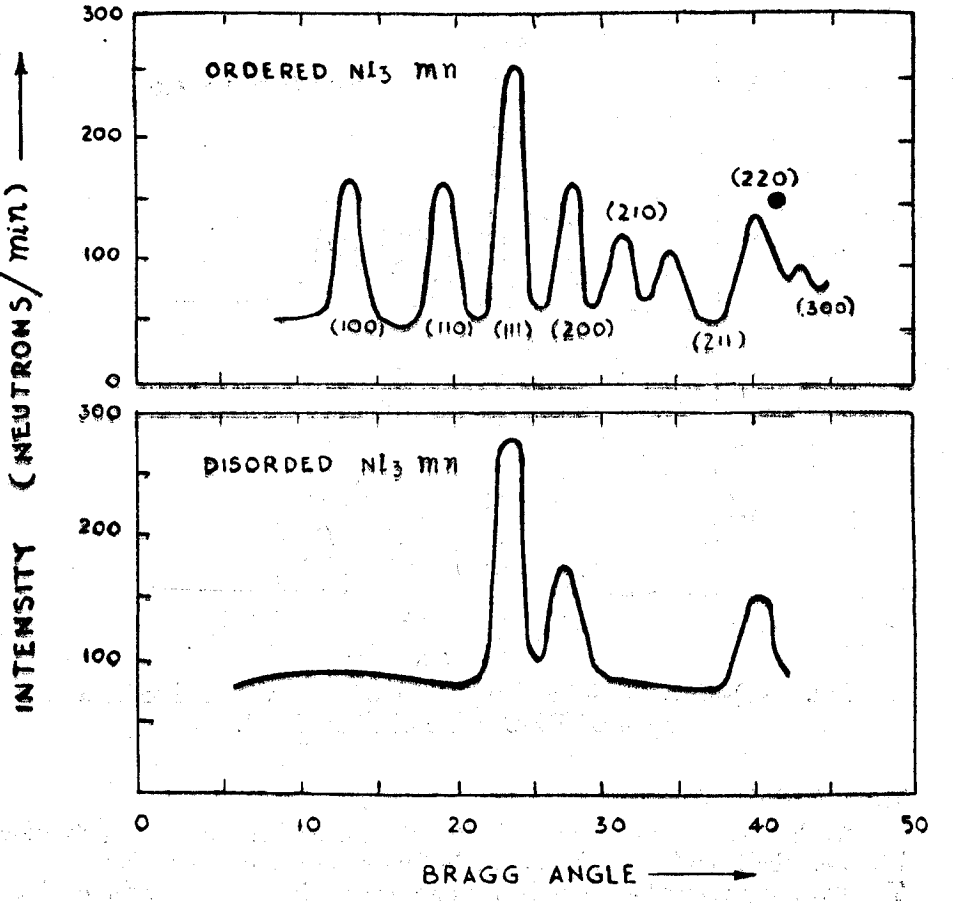

FIG. 4 (A)—Neutron diffraction patterns of ordered and disordered samples of Ni_3Mn.

In the case of $MgFe_2O_4$, X-rays could find the correct structure since Mg and Fe have different scattering powers for X-rays. In the case of Mg Al_2O_4 neutron scattering amplitudes of Mg and Al would not be so near as those for X-rays. Thus normal, inverse and intermediate stages could be easily distinguished by neutrons. Distinction between the 'normal' and 'inverse' structures for many ferrites (of spinel type) has been made by X-ray studies. The ferromagnetism in ferrites is associated with 'inverse' arrangement. Again in ferrites like $MnFe_2O_4$, Fe_3O_4, $CoFe_2O_4$, $NiFe_2O_4$ and $MgFeAlO_4$, X-ray measurements are inconclusive on account of similarity of scattering amplitudes of these metallic ions. The precise interpretation of diffraction intensities in MgFe AlO_4 is made more difficult by the fact that the oxygen parameter has also to be determined. The structure of these compounds can be studied by neutron diffraction as the metallic ions will have different scattering amplitudes (Bacon & Roberts[10]). Further, the scattering amplitude of oxygen for neutrons is greater than that of magnesium and aluminium and is as much as 60% of the value of iron, in contrast to its inferiority to that of metals in the case of X-rays.

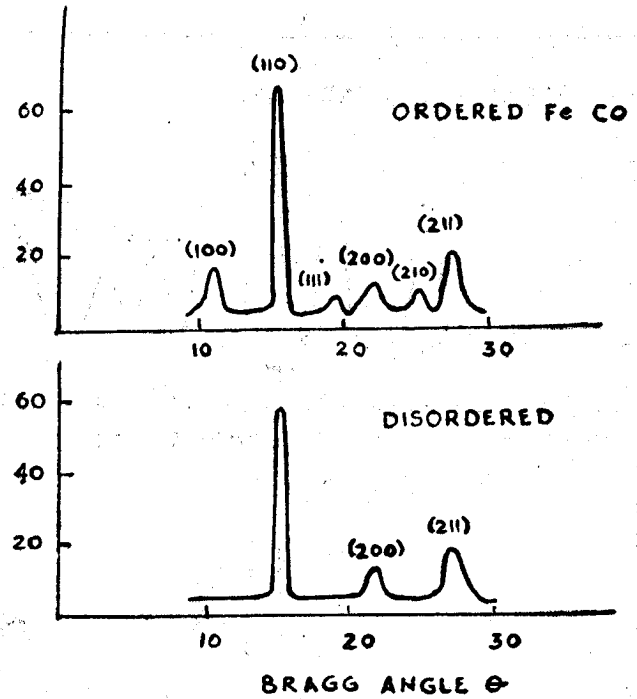

FIG. 4 (B)—Neutron diffraction pattern of ordered and disordered samples of FeCO. (after Shull & Siegel).

Magnetic Materials

At the present time the most significant contribution of neutron diffraction has been the knowledge gained from the investigations of magnetic materials. The magnetic properties as well as many other physical properties of these metals such as their crystal sturucture, lattice spacing, thermal expansion, compressibility etc. must be co-related at least by a satisfactory theory of the nature of the coupling between their atoms, and between atomic spins.

The powder diffraction pattern of polycrystalline iron (Fig. 5) has been investigated by Shull, Wollan and Koehler[11]. The pattern can be interpreted

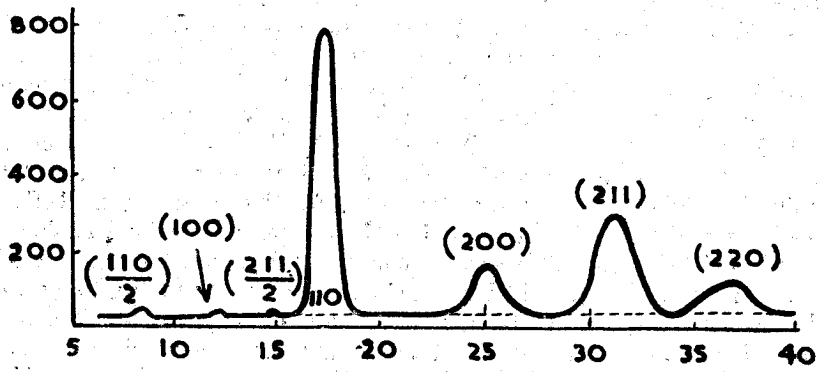

Fig. 5—Neutron diffraction powder pattern of iron (after Shull *et al*).

as being due to a superposition of the effects of the isotopic nuclear scattering by iron atoms and the magnetic scattering resulting from the magnetic moment of the atoms. It is of interest to examine this diffraction pattern in relation to the assumptions made in certain theories which try to account the magnetic moment of iron atom ($2 \cdot 2\,\mu_B$., μ_B is Bohr Magneton). According to Hume-Rothery *et al.*[12] this was a mean value due to an ordered arrangement of two types of iron atoms. Fe^{3+} ions with moment $5 \cdot 0\ \mu_B$ at cube corners and atoms with zero moment at the centre. This arrangement would give a magnetic moment of $5 \cdot 0 \mu_B$ per two atoms or $2 \cdot 5\ \mu_B$ per atom. According to Zener[13], two types of iron atoms having magnetic moments $5\ \mu_B$ and $1 \mu_B$ are arranged antiferromagnetically on the two types of sites. On this theory the magnetic moment would be $\frac{5\mu_B - \mu_B}{2}$ per atom. In either instance (100) superlattice line should be observed. The neutron diffraction pattern do not show any such line. The random distribution of the two types of magnetic moments should show no 'superlattice' line, but should show incoherent magnetic diffuse scattering of the kind shown by a paramagnetic material. Shull and Wilkins[14] carefully studied the diffuse scattering with and without magnetic field. The results showed that $\mu_1 - \mu_2$ could be greater than $0 \cdot 6\ \mu_B$ and hence disorder cannot explain magnetic moment of iron. Thus, neither order nor disorder could be explained experimentally. Stoner [15], Slator[16] and Pauling[17] have worked out theories on different assumptions. Certain of these cannot be verified by neutron diffraction and the others require advancement of this technique.

In addition to pure metals Shull and Wilkinson[14] have investigated a number of iron alloys (Co-Cr, Fe-Cr, Ni-Fe). The neutron method is advantageous for the alloy problem in that the magnetic moments associated with each of the constituent atoms can be determined separately.

In the case of Ni_3 Fe system, for which moments were determined for both ordered and disordered states, it was found that ordering had little or no effect on the individual moments. It is, thus, the overall composition of the sample which affects the individual moments rather than the immediate neighbour relations, these being the ones which are modified in the ordering process. Further results showed that the addition of Cr into either Fe or Co lowered the moments of the solvent atoms whereas the addition of Fe into Ni raises the Ni normal.

Ferro-electrics

An interesting class of materials exhibiting ferro-electricity on spontaneous electric polarisation has received considerable attention recently. At temperatures below ferro-electric Curie point, ionic displacements occur in an ordered fashion in the crystal structure, with the result that an electric dipole moment is produced within the unit cell. Since these displacements are ordered from one cell to another, within a ferro-electric domain, a microscopic electric polarisation is displayed by the substance. Diffraction is displayed by techniques which offer a method of direct measurement of these ionic displacements and combined with X-ray and neutron studies have served to determine the structural changes in a few cases.

Shirane *et al.*[18] have determined the structural changes associated with ferroelectric-transition in $PbTiO_3$. This compound exists in a cubic para-electric phase at temperatures above 490°C and in tetragonal ferro-electric phase below this temperature. In transition to tetragonal phase, several ions in the unit cell suffer displacements from the ideal position. Extensive X-ray and neutron data have shown that the positive ions are displaced from negative ions along the C axis in regular fashion and a net electric dipole results.

The electric and other physical properties of $BaTi0_3$ have been studied extensively by Kaenzig[19]. Barium titanate exhibits three ferro-electric phases. Possessing a cubic perovskite structure at high temperatures, $BaTiO_3$ transforms to a tetragonal modification at its curie temperature around 120°C, upon further cooling the symmetry changes to orthorhombic at 5°C and to rhombohedral at —80°C. The dielectric anomalies as well as the associated changes in physical properties are well established. The behaviour of $BaTiO_3$ through the three phase transitions can be explained by the single free energy function. (Devonshire[20]). This imposes however the restriction that any atomistic model proposed to explain the mechanism of the ferroelectric properties of $BaTiO_3$ must satisfy this thermodynamic requirement.

A knowledge of exact atomic positions in three phases, however, is necessary for understanding the ferro-electric behaviour of $BaTiO_3$. X-ray method is insensitive to the small ionic shifts from the cubic position, due to the small scattering factor of oxygen when compared with Ba or Ni. However, this difficulty can be removed by using neutron diffraction as in this case the scattering power of oxygen, Ba and Ti is of the same order.

A c-plate crystal ($12 \times 2 \cdot 5 \times 0 \cdot 38$ mm.) with an axis parallel to the length was used. (Frazer *et al.*[21]). Electrodes were applied to permit unidirectional domain allignment by an electric field during the neutron observations (350 volts across the c-plate). Scattering data were collected at wavelengths of $1 \cdot 063$ Å and $0 \cdot 905$ Å.

The projection of the structure of orthorhombic $BaTiO_3$ on (100) plane is shown Fig (6). With respect to barium at its origin, the titanium atom is displaced from its cubic position by 0·06 A in the positive Z direction. Oxygen atoms O_{II} which are coplaner with Ti atoms are shifted by $0 \cdot 07$ Å in opposite direction. In addition, the O_{II} have small shifts in y-direction such that their resultant displacement is towards Ti atom. The remaining 0_1 oxygen atoms are displaced in 'Z' direction. Since the choice of the origin is arbitrary along Z direction the structure can alternatively be described in terms of Ti and Ba atoms with respect to oxygen octahedra. These shifts result in large differences in the bond strengths between Ti and six surrounding oxygen ions. Recent Neutron diffraction studies by Shirane *et al.*[22] have cleared the structural compositions of the three phases of $BaTiO_3$. It is certain, now, that whatever the origins of ferroelectricity may be, they must be physical quantities which are changing gradually and continuously even through the phase transitions. The observed changes in Ti-O bond in $BaTiO_3$ do not necessarily imply that a change in the co-valent bond system is the 'origin' of ferro-electricity.

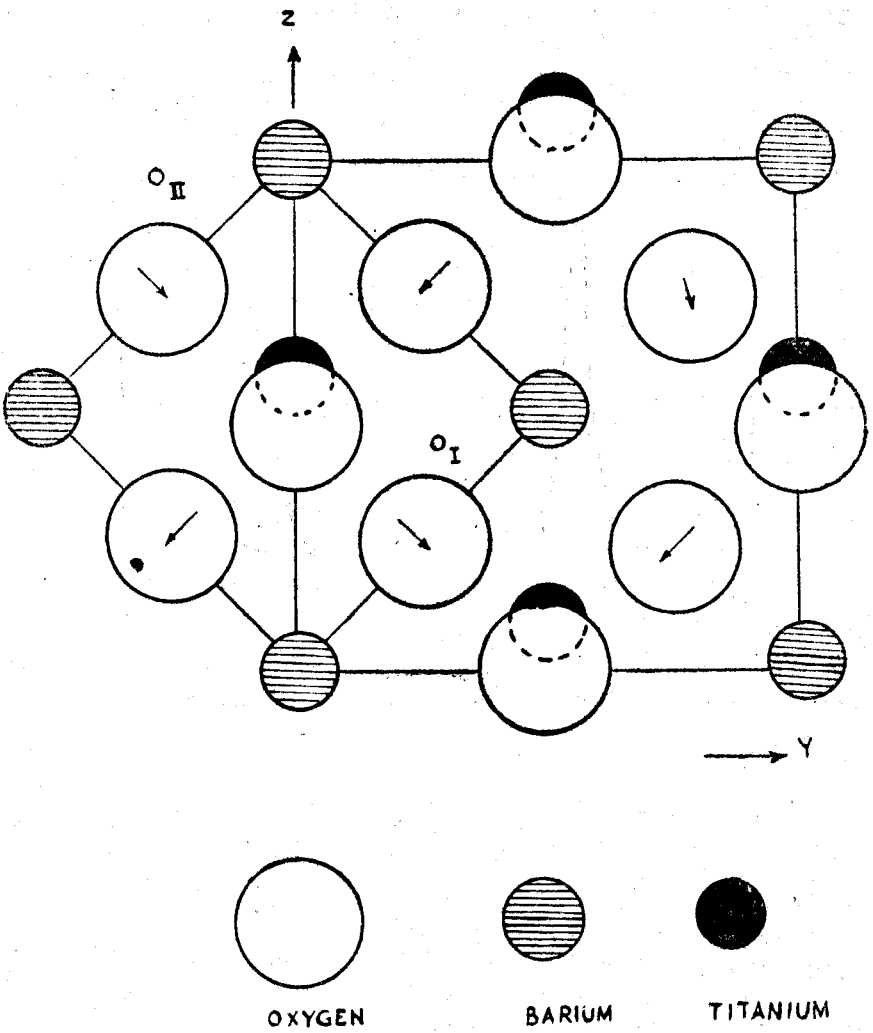

Fig. 6—Projection of $BaTiO_3$ on (100) plane.

The temperature dependence of the spontaneous polarisation was studied with the field applied along (110) direction. The spontaneous polarisation increases by about 40% on cooling through the tetragonal-orthorhombic phase transition. This combined with the reported drop along (100) direction (Merz[23]) can be considered a sufficient proof that the polars direction is (110).

Several neutron diffraction studies have been made to investigate the ferroelectric structure of KH_2PO_4. (Levy *et al.*[24], Pepinsky and Frazer[25]). A novel technique of studying hydrogen atom displacements in the ferroelectric state was used by Bacon and Pease[26]. This consisted of controlling the electrification vector and hence the ferro-electric displacements during the neutron scattering by applying an electric field to the crystal. Fig. (7) illustrates the (400) reflection in ferroelectric KH_2PO_4 as measured from a positive

and negative field direction. Reversing the field direction produces an interchange of the a and b axes of the orthorhombic unit cell, which changes (400) into a (040) reflection, with consequent structure factor and intensity modifications. The calculated crystal structure factor (400) and (040) reflections for the OH centre hydrogen lattice are in the ratio 1 to 8, and the intensities observed after field reversal are not inconsistent with this value.

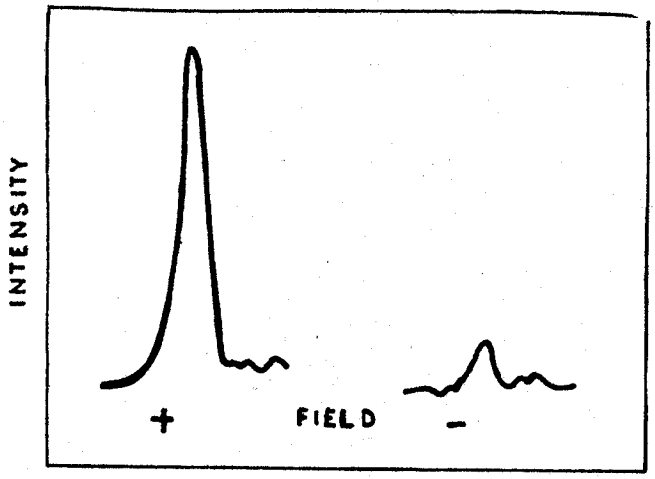

FIG. 7—Variation of Intensity of (400) reflection in ferroelectric KH_2PO_4 with reversal of applied electric field. (after Bacon & Pease)

Semi-conductors

Semi-conductors are electronic conductors with values of electrical resistivity at room temperature generally in the range $\sim 10^{-2}$ to 10^{9} ohms cm., intermediate between good conductors ($\sim 10^{-6}$ ohms cm.) and insulators ($\sim 10^{14}$ to 10^{22} ohms cm.). At absolute zero a pure and perfect crystal of most semi-conductors would behave as an insulator. The characteristic semi-conducting properties are usually brought about by thermal agitation (intrinsic semi-conductors) and by impurities or lattice defects (extrinsic semi-conductors). A number of devices of wide industrial applications are based on properties of semi-conductors. They include rectifiers, modulators, detectors, thermistors, photocells and crystal triode or transistors. The semi-conductors mostly used are silicon, germanium, Cu_2O, selenium, PbS, PbTe, SiC, etc.

For manufacturing these devices, the processes used have been worked out only by experience. In the case of copper oxide rectifiers, oxide is grown one copper at about 1030°C and then a certain heat treatment is given Dixit and Agashe[29] have shown that the oxide formed by the above process is semi-conducting but the rectification is obtained only after heat treatment. By adjusting heat treatment suitably, rectifiers of different characteristics can be obtained. In the case of selenium rectifier, a heavy electric current has to be passed through the opposite direction, after which the selenium cell works as a rectifier. This is called forming of selenium rectifier. Germanium and silicon have to be

purest (one in 10^{10} atoms) and proper impurities (As, P etc.,) are to be introduced in it. Welkar[27] by preparing a number of III—V group compounds has shown a connection between semi-conduction (and rectification) and crystal structure. 'The compounds showing a diamond type of structure show rectification.' Germanium and silicon exhibit a diamond lattice. Hoffman and Rose[28] have shown that the selenium layer (after forming) has a zinc sulphide type of structure (zinc sulphide structure is identical to diamond if all atoms were the same). Dixit and Agashe[29] have shown that the copper oxide rectifying layer is also nearer to zinc sulphide in structure than pure Cu_2O. (Cu atoms on F.C.C. lattice and oxygen atom on B.C.C. lattice both of side 4·26 A).

The addition of boron to silicon and arsenic or phosphorous to germanium increases the conductivity. In the case of stoichiometric compounds (Cu_2O, ZnO, etc.) excess or deficiency of one constituent causes the change in conduction. The foreign atoms or excesses/deficiencies of a constituent enter the lattice by substitution. Grain size, distribution of impurities (or vacancies) and plausible changes in the crystal structure of these semi-conductors are important in understanding their properties. X-ray scattering of Ge and As is nearly the same (Table 1), while neutron scattering amplitudes are different. In the case of copper oxide, oxygen parameter and/or copper vacancy have to be determined. For X-rays the scattering amplitude of oxygen would be much inferior to that of copper, while with neutrons, oxygen scattering is about 75% of the value of copper. The high absorbing power of neutrons in the case of boron may also be useful in detecting position of boron with respect to silicon atom. X-rays. and electron diffraction methods in determining the crystal structure have not completely succeeded. Certain advantages of neutrons diffraction (as discussed) are likely to give more information about these materials. Neutron diffraction coupled with X-ray and electron diffraction will be able to give us a complete picture of the crystalline state of these materials especially in the form in which they are used in modern devices and thus help us in understanding the physics of these devices.

Conclusion

From the above discussion of neutron diffraction technique as applied to problems in physics and metallurgy, it is clear that this technique is complementary to X-ray technique. It is useful especially when, X-ray method fails. However, it must be emphasised that neutron diffraction technique, in its present form, cannot supersede X-ray diffraction technique. With the available pile powers and methods of neutron detection, the experimenter has to make a compromise between a large neutron counting rate (for high accuracy) and rapid measurement. The high resolution is essential in order to obtain discrete spectra free from overlapping. The output of an X-ray tube is usually sufficient to give adequate intensity and resolution at the same time. The number of quanta per unit area in normal X-ray beam is greater than those in neutron beams by a factor of about 10^5. It must be borne in mind that at the present stage of development, volume of specimen required for neutron diffraction work is much larger than the volume required for X-ray diffraction study. This necessitates larger single crystals for neutron diffraction which is rather difficult. Further improvements can, however, be expected as the technique has been developed but recently.

References

(1) Elasasser, W.M., *C.R. Acad. Sci.* Paris, **202**, 1029, 1936.

(2) Bacon, G.E. and Thewlis, J., *Proc. Roy . Soc.*, A **196**, 50, 1949.

(3) Wollan, E.O. and Shu, G.C., *Phys. Rev.*, **73**, 830, 1948.

(4) Sturm, W.J., *Phys. Rev.*, **71**, 757, 1947.

(5) Shull, C.G. and Wollan, E.O., *Phys. Rev.*, **81**, 527, 1951.

(6) McReynolds, A.W., *Phys. Rev.*, **88**, 958, 1952.

(7) Fowler, I.L. and Junnicliffe, P.R., *Rev. Sci. Instrum.*, **21**, 734, 1950.

(8) Wollan, E.O., Shull and Marney, M.C., *Phys. Rev.*, **73**, 527, 1948.

(9) Verwey, E.J.W. and Hilman, E.L., *J. Chem. Phys.*, **15**, 174, 1947.

(10) Bacon, G.E. and Robert, F.F., *Acta Cryst.*, **6**, 57, 1953.

(11) Shull, C.G., and Wollan and Koehler, W.C., *Phys. Rev.*, **84**, 912, 1951.

(12) Hume Rothery, W., *J. Inst. Metals*, **35**, 295, 1934.

(13) Zener, C., *Phys. Rev.*, **85**, 324, 1952.

(14) Shull, C.G., and Wilkinson, M.K., *Rev. Mod. Phys.*, **25**, 100, 1953.

(15) Stoner, E.C., *J. Phys. Radium*, **12**, 372, 1951.

(16) Slator, J.C., *Rev. Mod. Phys.*, **25**, 211, 1953.

(17) Paling, L., *Proc. Roy. Soc.*, A **196**, 343, 1949.

(18) Shirane, G. Pepinsky, R and Fraser, B.C., *Acta Crystal*, **9**, 131, 1956.

(19) Kaenzig, W., *Phys. Acta.*, **24**, 175, 1951.

(20) Devonshire, A.F., *Phil Mag.*, **40**, 1040, 1949; **42**, 1065, 1951.

(21) Frazer, B.C., Danner, H.R. and Pepinsky, R., *Phys. Rev.*, **100**, 745, 1955.

(22) Shirane, G., Danner, H., Pepinsky, R., and Frazer, B.C., *Phys. Rev.*, **105**, 856, 1957.

(23) Merz, *Phys. Rev.*, **76**, 122, 1949.

(24) Levy, H.A., Peterson, S.W. and Simonsen, S.H., *Phys. Rev.*, **93**, 1120, 1954.

(25) Pepinsky, R. and Frazer, B.C., *Science*, **117**, 1, 1953.

(26) Bacon, G.E. and Peace, R.S., *Proc. Roy. Soc.*, A **220**, 397, 1953; A 230, 359, 1957.

(27) Welkar, H. *Z., Naturforsch*, **7a**, 744, 1952; **8a**, 248, 1953.

(28) Hoffman, A. and Rose, F., *Z. Phys.*, **136**, 152, 1953.

(29) Dixit, K.R. and Agashe, V.V., *Z. Naturforsch*, **10a**, 152, 1955; **12a**, 96, 1957; *Ind. J. Phys.*, **31**, 466, 1957.