

CONF-8509288--1

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EARLY HISTORY OF NEUTRON SCATTERING AT OAK RIDGE

CONF-8509288--1

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Prepared by the
SOLID STATE DIVISION
OAK RIDGE NATIONAL LABORATORY
Operated by
Martin Marietta Energy Systems, Inc.
for the
U.S. DEPARTMENT OF ENERGY
Oak Ridge, Tennessee

July 1985

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EARLY HISTORY OF NEUTRON SCATTERING AT OAK RIDGE

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ABSTRACT

Most of the early development of neutron scattering techniques utilizing reactor neutrons occurred at the Oak Ridge National Laboratory during the years immediately following World War II. C. G. Shull, E. O. Wollan, and their associates systematically established neutron diffraction as a quantitative research tool and then applied this technique to important problems in nuclear physics, chemical crystallography, and magnetism. This article briefly summarizes the very important research at ORNL during this period, which laid the foundation for the establishment of neutron scattering programs throughout the world.

1. Introduction

In this Ceremonial Conference honoring Professor Clifford Shull, it is particularly appropriate to include a review of the early history of neutron scattering at Oak Ridge. Most of the early development of this important field of research took place at the Oak Ridge National Laboratory in the years immediately following World War II, and the contributions of Professor Shull were an enormous part of this development. In fact, those of us who have been associated with neutron scattering for many years are still somewhat amazed at the speed with which this development occurred and at the breadth of problems to which the technique was applied in those early days.

Of course, the neutron was discovered by Chadwick in 1932, and this discovery was quickly followed by many theoretical and experimental investigations to study the interactions of this new form of radiation with nuclei and to establish its physical properties. The major sources of neutrons in those days were radium-beryllium sources that provided relatively low intensity beams of heterogeneous neutrons. Therefore, even though it was possible to demonstrate the diffractive properties [1,2] of neutrons, the low intensities did not permit work on any practical problems. In the pre-reactor days there was also considerable research activity associated with the magnetic scattering of neutrons, which was stimulated primarily by calculations of Bloch [3]. These calculations showed that the interaction of neutrons with magnetic atoms resulted in a cross section comparable in size to nuclear cross sections and suggested a method of producing polarized neutron beams by transmission through a magnetized sample.

Although this early activity was extremely important, the field of neutron scattering did not really begin to flourish until the development of nuclear reactors, which provided neutron beams of sufficient intensity that

quantitative measurements of the scattered neutrons could be made. The work at ORNL was initiated by E. O. Wollan in late 1945, and he was joined several months later by Professor Shull. The work by these two scientists and their associates laid the foundation for the widespread application of neutron scattering techniques throughout the world and for the preeminent position that these techniques have established in many areas of scientific research. It is the purpose of this article to summarize the very important developments in neutron scattering that were part of Professor Shull's career at ORNL from 1946 to 1955.

2. Experimental Facilities

The early neutron scattering work at ORNL was performed at the Oak Ridge Graphite Reactor, which became operational in November 1943 and remained in operation until November 1963. This reactor was a large air-cooled, graphite-moderated "pile" of natural uranium fuel, which produced a neutron flux about 10^{12} neutrons/cm² s. The first experiments involving the diffraction of reactor neutrons were performed at both Oak Ridge National Laboratory and Argonne National Laboratory, and they utilized single-axis instruments to obtain monoenergetic neutron beams for total cross section measurements. These experiments were soon followed by double-scattering investigations, in which monoenergetic neutrons from one crystal were scattered from a second crystal to obtain information on the coherent scattering characteristics of particular atoms.

The first two-axis instrument that was used for neutron diffraction research was installed at the Oak Ridge Graphite Reactor by Wollan and his associates in November 1945. A photograph* of this diffractometer is shown in

*This photograph was taken in 1948 after several stages of improvement.

Fig. 1. The second axis was an x-ray instrument that Wollan had used at the University of Chicago, and it was modified in the ORNL shops so that it could be used for neutron work. The diffractometer was not capable of supporting the large shielding required around the detector, and support cables were attached to a ceiling support bearing. Data were first taken by hand positioning of the detector, and because of high neutron background, considerable time was spent measuring the background with a small piece of cadmium inserted as a shutter for the incident beam. In early 1947 an automatic control system was added, by which the detector was moved in steps and the data for a specific time interval were recorded on a traffic counter; alternate intervals were provided with the cadmium shutter in the incident beam. The first version of this diffractometer had shielding of paraffin blocks and cadmium sheeting around the detector and a rather poor monochromator shield built with paraffin blocks and lead bricks.

The first two-axis diffractometer, which was designed exclusively for neutron diffraction, was built in the ORNL shops and installed in July 1950 at a beam port of the Oak Ridge Graphite Reactor adjacent to the modified x-ray instrument. A photograph of this instrument, which was taken with Wollan and Shull in attendance shortly after the installation, is shown in Fig. 2. This diffractometer was a very flexible instrument, and it was the first to use a rotating-drum shield around the monochromating crystal, so that neutron wavelengths could be adjusted continuously. The instrument was also sufficiently sturdy that it could support the detector and detector shield as well as auxiliary apparatus, such as magnets and cryostats, for changing the sample environment.

3. Early Development of Techniques

In all of the very early neutron scattering studies at ORNL, large single crystals of rock salt were used as monochromating crystals. Moreover, as stated previously, the first experiments also used large single crystals as the scattering samples. However, because of extinction effects, very inconsistent results were obtained for different crystals and even for equivalent orientations of the same crystal. In April of 1946, the first neutron powder pattern was obtained. This pattern, which is shown in Fig. 3, was taken for a 1-cm-thick pressed briquet of polycrystalline NaCl. The monochromatic beam incident on the sample, which was obtained from a NaCl monochromator, had a wavelength of about 1.05 \AA and a cross-sectional area of about 8 cm^2 . The high background in the pattern was due primarily to instrumental background, and it was later improved significantly by better shielding. In spite of the very low intensities in the diffracted beams, it soon became apparent that reliable measurements could be made of the absolute integrated intensities from powdered crystals.

Between 1946 and 1948, Skull, Wollan, and their collaborators systematically investigated the fundamentals of thermal neutron scattering by crystalline powders. Both of these scientists had strong backgrounds in x-ray physics, and they were able to develop this technique with surprising speed. It must be remembered that all neutron scattering amplitudes have to be determined experimentally, and of course, before the first one could be measured with any confidence, neutron scattering measurements had to be placed on a firm absolute intensity scale. This meant untangling effects associated with bound and free nuclei, nuclear spin incoherence, isotopic incoherence, and thermal diffuse scattering, in addition to various instrumental problems such

as multiple scattering. To indicate how rapidly they were able to deal with these problems, it is only necessary to mention the early literature. The research was first discussed [4] at the Washington meeting of the American Physical Society in May 1947, and the first publications appeared in 1948. The latter consisted of a description [5] of the technique; a determination [6] of the neutron-proton scattering amplitude and the range of nuclear forces in the neutron-proton interaction; an investigation [7] of hydrogen atom positions in crystal structures; observations [8] of the first Laue photographs; and three review articles [9].

An account of the early history of neutron scattering at Oak Ridge would be incomplete without some indication of the trials and tribulations of this two-year period, and some of the highlights will be mentioned. For a more complete picture of this period, reference should be made to a presentation [10] by Professor Shull at the Conference on Neutron Scattering held in Gatlinburg, Tennessee, June 6-10, 1976.

Of course, one of the first problems addressed was improvement of the diffractometer. Considerable effort was spent in realigning the instrument to improve the low counting rates in the scattered beams and in improving the shielding to reduce the background; a significant increase was obtained in the signal-to-background ratio. Attention was then turned toward careful measurements of the diffraction intensities from polycrystalline NaCl and KCl. The ratio of the coherent scattering cross sections for Na and K obtained from these measurements was compared with the ratio of the total scattering cross sections obtained from transmission measurements with corrections for capture. These early comparisons gave discrepancies that were attributed to nuclear spin and isotopic incoherence, and the investigations quickly turned to powders of CaO, CaS, and CaC₂, which contained atoms with zero nuclear spin

and a single isotope. The observed diffuse scattering in these experiments was very large, and again the relative coherent scattering cross sections were not consistent with the total scattering cross sections. Because of uncertainties about the compounds, an additional step was taken to simplify the experiments. Measurements were made on a single element, carbon, which is monoisotopic with zero spin, in the forms of diamond dust, graphite powder, and amorphous charcoal. The interpretation of these patterns also turned out to be difficult; the diffuse scattering was large, and there were problems in accounting for all of the scattering. Of course, very little was known about neutron scattering at this time, and there was much speculation concerning possible reasons for these inconsistencies. The solution to the problem came in mid-1947, when it was established that the large observed diffuse scattering was caused by multiple scattering in the specimens. After correcting the diamond measurements for multiple scattering, the remaining diffuse scattering could be explained by temperature effects. Based on this understanding of the scattering from carbon, it was then possible to put the various types of nuclear scattering on a quantitative basis and to interpret neutron diffraction intensities with confidence.

At the same time that the early powder diffraction studies were made, Shull and Wollan were also interested in obtaining photographs of diffraction patterns. The first clear image Laue pattern was obtained [8] from a NaCl crystal, and this pattern is shown in Fig. 4. It was obtained with a white beam of neutrons about 6 millimeters in diameter and recorded on x-ray film with an indium sheet placed adjacent to the film; the exposure time was about 16 hours. As Professor Shull has pointed out [10], this pattern also shows the first radiographic imaging with neutrons. Since an indium sheet of sufficient area was not available at the time, several strips had been taped

together with Scotch tape, and there is a clear neutron imaging of this tape in the photograph. The doubling of the neutron spots in the pattern turned out to be an artifact associated with mosaic layers on both faces of the NaCl crystal. Shull and Wollan took Laue photographs of many other single crystals that were available at ORNL, and these photographs were very important in the development of neutron scattering techniques. It was obvious from the photographs that the integrated intensities in the diffraction spots from metallic crystals were much larger than those from NaCl, which immediately suggested the use of metal crystals for monochromators. The NaCl monochromating crystals were replaced by metallic crystals in early 1948, and such crystals have been used extensively in neutron scattering research since that time.

4. Nuclear Physics Research

One of the first major contributions of neutron diffraction to nuclear physics was the measurement [6,7] of the coherent scattering amplitude of hydrogen using a sample of powdered NaH. This measurement was important because it involved the interaction between two fundamental particles and was therefore a problem that could receive a thorough theoretical treatment. From the value of the coherent scattering amplitude and the free-proton scattering cross section [11], it was possible to evaluate the scattering amplitudes characteristic of the individual singlet and triple states. These data and earlier experiments on the scattering of slow neutrons by ortho- and para-hydrogen showed that the interaction of the proton and neutron is strongly dependent on the relative orientation of the spins of the two particles. Furthermore, it was possible to obtain a value for the range of the neutron-proton triple interaction. A subsequent investigation on a number of deuterium-containing compounds [12] gave an accurate measurement of the

neutron coherent cross section of deuterium, which was used to determine the spin-dependent neutron deuteron scattering amplitudes.

In an attempt to furnish background for the development of nuclear theory, much of the early research of Shull, Wollan, and their associates involved the systematic measurement of the neutron scattering properties of nuclei in a large number of materials. These measurements were a very significant contribution and undoubtedly represent some of the most important research performed at ORNL during that period. A major review article [13] appeared in 1951, which contained results of these nuclear scattering studies; the phase of scattering and values for the coherent scattering amplitude, coherent scattering cross section, and total scattering cross section were given for over sixty elements and isotopes. Pronounced differences were shown to exist in isotopic scattering properties, and many nuclides were found to possess scattering properties that were strongly dependent on the nuclear spins. These measurements, of course, were necessary for future crystallographic structure studies, but they were also of importance in nuclear physics. For example, both the magnitude of the scattering cross section and the sign of the scattering amplitude provided information concerning the effects of resonance scattering by the nucleus.

These resonance effects were demonstrated very dramatically by an investigation of the coherent neutron scattering cross section of nickel and its isotopes [14]. This study was of particular interest at the time, because the scattering data from normal nickel had indicated that the scattering properties of the nickel isotopes would be widely different. Portions of the diffraction patterns that were taken for samples of NiO enriched in Ni⁵⁸, Ni⁶⁰, and Ni⁶², compared with NiO, are shown in Fig. 5. Since NiO has the rock salt structure, it was very easy to determine the phase of scattering of

the nickel samples relative to oxygen; all scatter with the same phase as oxygen except Ni⁶². These data also indicated a virtual resonance for Ni⁵⁸ and positive energy resonances for Ni⁶⁰ and Ni⁶².

5. Chemical Crystallography

Although much of the very early neutron scattering work at ORNL was directly concerned with nuclear physics, values of the coherent scattering cross sections had quickly revealed the tremendous potential of neutron diffraction for crystal structure determinations, and particularly for hydrogen atom crystallography. One of the first investigations of this type was a determination of the crystal structure of ice; this investigation was first mentioned in an ORNL progress report of September 1947, but it was not published [15] until a later date. The oxygen atom positions had already been determined from x-ray measurements, but the hydrogen positions were unknown. Four structures had been proposed for the location of the hydrogen atoms, and they are shown in Fig. 6. These structures were (a) the Barnes model, in which the hydrogen atoms are midway between oxygen atoms; (b) the Bernal and Fowler model, which maintains a molecular grouping of two hydrogen atoms close to each oxygen atom with a definite repeating orientation; (c) the Pauling half-hydrogen model, in which two hydrogen atoms are associated with a particular oxygen atom, but each hydrogen atom divides its time between two positions along the oxygen linkages; and (d) a model consisting of hydrogen molecules rotating around the oxygen atoms as centers. The neutron diffraction measurements were made on a powdered sample of heavy ice (D₂O), and although the intensities and resolution were limited, it was clear that only the Pauling model agreed with the data.

This work on ice, which was followed by a collaboration with R. E. Rundle on the crystal structure of thorium and zirconium dihydrides [16], was of such

interest to crystallographers at ORNL that a separate program was initiated by H. A. Levy to investigate hydrogen bonding in materials by neutron diffraction techniques. Levy and Peterson at ORNL and Bacon at AERE, Harwell, pioneered the single crystal technique of neutron crystallography for detailed structural analysis. The first hydrogen-bonded compound to be investigated by single crystal methods was KHF_2 , in which Peterson and Levy [17] showed that the F-H-F bond is symmetrical with no detectable departure from spherical symmetry in the vibration of the proton. It should also be mentioned that these scientists later performed a detailed single-crystal investigation of ice [18], which confirmed the half-hydrogen model that had been determined from the early powder data.

Another very early study in chemical crystallography at ORNL involved order-disorder phenomena in binary alloys. Considerable work of this type had been performed by x-ray diffraction techniques, but a number of important alloy systems could not be studied with x-rays. The sensitivity of diffraction techniques in such studies depends on the difference in scattering power of the atoms involved, and the regular variation of x-ray scattering amplitudes with atomic number made certain investigations impossible. The early neutron diffraction experiments [19] were made on FeCo, Ni_3Mn , and Cu_3Au ; the results clearly indicated the value of neutron diffraction for experiments of this type.

6. Magnetic Neutron Scattering

One of the most important applications of neutron scattering has been the investigation of magnetic phenomena, because it is a unique tool for determining information about magnetic materials. Shull, Wollan, and their associates moved into this area very quickly after they had put neutron diffraction techniques on a firm foundation. Because of the great interest in nuclear physics and in new types of crystallographic problems, this early turn toward

the field of magnetism might seem somewhat surprising. However, a brief review of the pre-reactor investigations of magnetic neutron scattering can help to clarify the path that was taken.

As stated in the Introduction, the early theoretical work of Bloch [3] had stimulated much activity in this area by showing that the magnetic scattering cross section was comparable in size to the nuclear scattering cross section and by suggesting a method of producing polarized neutron beams by transmission through a magnetized sample. Whereas these calculations had assumed that the neutron could be treated as a magnetic dipole, Schwinger [20] obtained somewhat different results by considering the neutron as an Amperian current. Bloch [21] then pointed out that the scattering from a ferromagnet would show a different angular dependence for the two cases and suggested that the distinction could be made by an experiment. Unfortunately, definitive experiments could not be performed because of the low intensity of thermal neutron sources. The calculations by Bloch and Schwinger had been based specifically on iron atoms in ferromagnetic metallic iron, but Halpern and Johnson [22] subsequently suggested that neutron scattering from other types of magnetic ions in a paramagnetic state might result in a more favorable experiment. The latter papers were then followed by three extremely important papers [23] by Halpern and his associates, which have formed the basis for essentially all experimental research involving magnetic scattering. These papers discussed the theoretical aspects of nuclear and magnetic scattering, coherent and incoherent scattering, and the polarization and depolarization of neutrons transmitted through ferromagnetic materials. Although these scientists believed that the Schwinger interpretation of the magnetic interaction was correct, they also thought that the distinction between the two interpretations should be made by experiment.

All of the calculations by Halpern and his associates had taken place at New York University at the time when Professor Shull had been in graduate school there. Moreover, many of the early attempts [24] to study these effects experimentally using weak Ra-Be sources had also been performed at that university. Consequently, even though his thesis research had been in a different area of physics, Professor Shull was thoroughly familiar with the work on magnetic neutron scattering and with the excitement that it had caused. Of course, he was also familiar with the limited success of the early experiments. Therefore, he was quite anxious to study the magnetic scattering phenomena with more intense neutron beams, and it was through his strong guidance that the early ORNL experiments were performed. These experiments provided information that explained important concepts in the field of magnetism, and they paved the way for many more sophisticated experiments that have been conducted throughout the world since that time. Much of the early work was published in short letters, but two major papers [25,26] published in 1951 contain most of the results of these early magnetic scattering investigations.

The first experiments at ORNL on magnetic scattering followed the suggestion by Halpern and Johnson to study ions in a paramagnetic state. These experiments were made at room temperature on a series of salts containing divalent manganese. According to the formulation of Halpern and Johnson, this ion would have a differential magnetic scattering cross section in the forward direction larger than the coherent nuclear differential scattering cross section. Diffraction patterns were obtained [25] for MnO , MnF_2 , and $MnSO_4$, and after corrections of the diffuse scattering for all other components, the resultant paramagnetic scattering was placed on an absolute scale as shown in Fig. 7. It was recognized at the time that the peaking in the data for MnO was unusual for an atomic form factor and that it was characteristic of some

form of short-range order. The other two curves portrayed the more normal dependence with scattering angle, and the form factor for Mn^{2+} was obtained from these curves. This form factor was then Fourier transformed to get the first experimental radial distribution function of the 3d-magnetic electrons in Mn^{2+} . This distribution function compared satisfactorily with a theoretical calculation by Dancoff [27], who used a self-consistent field analysis with exchange effects included.

As stated in a recent review article by Professor Shull [28], during this period of research, he was informed of Professor L. Néel's work on magnetic materials [29] by L. Maxwell and J. S. Smart of the U.S. Naval Ordnance Laboratory. Néel's papers immediately suggested that the peaking in the diffuse scattering from MnO was probably due to short-range magnetic order and that long-range order might develop below an antiferromagnetic ordering temperature of 122 K. The work of Néel also suggested an explanation for extra diffraction lines that had been observed in a neutron diffraction pattern of $\alpha\text{-Fe}_2\text{O}_3$ at room temperature. Néel had indicated that $\alpha\text{-Fe}_2\text{O}_3$ would be antiferromagnetic below 950 K, and it was quite probable that the extra diffraction lines at room temperature were a result of long-range antiferromagnetic order. Of course, both low-temperature and high-temperature diffraction patterns were obtained for MnO and $\alpha\text{-Fe}_2\text{O}_3$, and these patterns [25,30] confirmed the existence of antiferromagnetism in both compounds at low temperatures. It should also be pointed out that the magnetic reflections in the diffraction pattern for $\alpha\text{-Fe}_2\text{O}_3$ at 80 K were different from those at room temperature, even though there was no crystallographic transition. It was established [25] that an anisotropy transition existed at about 253 K, which caused a reorientation of the direction of the magnetic moments.

The early neutron diffraction investigation of MnO is really a classic, and the original data at 293 K and at 80 K are shown in Fig. 8. The room temperature pattern has diffraction peaks at the regular face-centered cubic positions and a liquid-type diffuse scattering characteristic of short-range order. The low-temperature pattern has the same nuclear diffraction peaks, which indicates no crystallographic transition at this temperature, and in addition, strong magnetic reflections exist at positions not allowed on the basis of the chemical unit cell. The magnetic structure shown in the figure was determined directly from the pattern; the specific orientation of the moments in a direction parallel to the (111) plane was determined in later investigations [31]. Of particular importance in this magnetic structure of MnO is the fact that the antiferromagnetic coupling between moments of the manganese atoms must be of an indirect type through an intermediate oxygen atom. Therefore, this result was the first experimental verification of the phenomenon of superexchange.

In addition to the investigation of MnO, neutron scattering studies were made [25] on other isomorphous oxides of the transition elements, FeO, CoO, and NiO. These oxides were also found to become antiferromagnetic at low temperatures with the same type of magnetic structure as MnO. The antiferromagnetic intensities corresponded to magnetic moments with both orbital and spin components, but with partial quenching of the orbital components.

With confirmation of the Halpern and Johnson theory as it applied to paramagnetic and antiferromagnetic scattering, the work at ORNL quickly turned to other types of magnetic materials, the most notable of which was magnetite, Fe₃O₄. This compound contains both Fe²⁺ and Fe³⁺ ions that are distributed among tetrahedral and octahedral sites. Néel [29] had suggested a magnetic structure, which he referred to as ferrimagnetic, in which the Fe moments on

tetrahedral and octahedral positions were coupled antiferromagnetically, but the two did not balance, thereby leaving a net ferromagnetism. This postulated structure was quickly confirmed by neutron diffraction measurements [26,32], assuming an inverted spinel in which the octahedral Fe sites are occupied at random by equal numbers of divalent and trivalent ions and the tetrahedral sites are occupied only by trivalent ions.

Two reflections from magnetite were found to be of very significant interest. The (111) reflection was determined to be almost completely magnetic in origin with only about a two percent contribution from nuclear scattering. Since the material is macroscopically ferromagnetic, the orientation of the moment direction could be controlled by an external magnetic field, which permitted studies of the directional properties of magnetic neutron scattering. In particular, the (111) reflection was used in a sensitive test to distinguish between the Bloch and Schwinger interpretations of the fundamental magnetic scattering interaction. The (111) powder diffraction ring of Fe_3O_4 was investigated [32] when the sample was magnetized in different directions, and typical results are shown in Fig. 9. For the situation in which the external field aligned the atomic magnetic moments parallel to the scattering vector, there was no magnetic scattering. When the direction of the atomic magnetic moments was perpendicular to the scattering vector, the intensity of magnetic scattering was a maximum and 50% greater than that for the unmagnetized sample. More specifically, the intensity was found to be proportional to the square of the sine of the angle between the magnetization and scattering vectors, a result that readily confirmed the Schwinger formulation. In this early investigation the possible application of a magnetic reflection of this type for a fast neutron shutter was suggested, although the actual development of such a shutter did not occur for a number of years [33].

Whereas the (111) reflection from magnetite was almost entirely magnetic, the (220) reflection was found to have almost equal magnetic and nuclear scattering amplitudes. Specifically, the nuclear scattering amplitude was 0.95×10^{-12} cm, whereas the magnetic scattering amplitude was 0.97×10^{-12} cm. Since exact equality of these amplitudes is the condition for 100% polarization of the reflected neutron beam, it was apparent that a very highly polarized beam could be obtained from this reflection, and as soon as a single crystal of Fe_3O_4 became available, the polarization was studied [34]. The crystal was placed in an external magnetic field perpendicular to the plane of scattering, and the degree of polarization in the reflected beam was determined by passage through a block of polycrystalline iron that could be magnetized in a separate and parallel field. Analysis of the data showed that the polarization was 100 percent within an experimental uncertainty of about 5 percent.

Similar experiments were performed on the polarization produced in the (110) reflection from an Fe single crystal. However, the measured value of 41% polarization was considerably lower than the calculated value of 60%. This discrepancy was explained on the basis of extinction effects, depolarization, and silicon impurities in the crystal. Other experiments involving ferromagnetic materials [26] were performed on polycrystalline samples of Fe and Co as a further check of the magnetic scattering theory. The results were found to be consistent with atomic magnetic moments determined in magnetization experiments and with the magnetic form factor calculated by Steinberger and Wick [35].

After these early experiments had shown the tremendous power of neutron scattering for investigating the magnetic properties of materials, most of the ORNL neutron scattering program under Shull and Wollan from 1951 to 1955 was directed toward problems that existed in understanding the magnetic behavior

of materials. This work included the first neutron scattering investigations of the magnetic properties of rare-earth oxides [36] and rare-earth metals [37]; investigations of antiferromagnetism in manganous fluoride and some isomorphous compounds [38]; a determination [39] of the magnetic structure of Mn_2Sb ; a detailed analysis [40] of the magnetic properties of the series of perovskite-type compounds $[(1-x)\text{La},x\text{Ca}]\text{MnO}_3$; investigations of the magnetic structure in 3d-transition metals [41] and alloys [42]; and investigations [43,44] of the high temperature and critical scattering from iron.

During this period Professor Shull became particularly interested in understanding magnetism in the 3d-transition metals and alloys. Although there had been speculation concerning the possibility of antiferromagnetism in the nonferromagnetic iron group metals, the first direct evidence was obtained by his neutron diffraction experiments [41] at ORNL. These experiments, which were performed on powdered specimens, showed that both chromium and alpha-manganese became antiferromagnetic at low temperature. The diffraction patterns that were obtained for $\alpha\text{-Mn}$ at both room temperature and 20 K are shown in Fig. 10. Although the superlattice reflections were readily apparent at the low temperature, it was not possible to determine a specific antiferromagnetic structure. A later detailed investigation [45] found the magnetic structure to be very complex, which is probably the result of the unusual crystal structure of this material. The early data on powdered chromium were consistent with a simple body-centered antiferromagnetic structure, but later single-crystal measurements [46] showed that the magnetic structure was more complicated.

Prior to the investigation at ORNL of 3d-transition-metal alloys [42], the main experiments in this field had been magnetic measurements, which are representative of the macroscopic average of the moments and offer no information on the individual atomic magnetic moments. However, the analysis of

magnetic neutron scattering from either ordered or disordered alloys, when combined with magnetization data, was found to provide information on the individual moments. In this early investigation at ORNL, measurements were made on ordered and disordered binary alloys in the Fe-Cr, Ni-Fe, Co-Cr, and Ni-Mn series of alloys. The results showed conclusively that different atomic magnetic moments exist in both the ordered and disordered alloys and that the values of the moments deviate from the elemental values as a function of alloy composition.

One of the last major neutron scattering investigations undertaken by Professor Shull before he left ORNL involved measurements of the magnetic properties of iron at high temperatures [43]. Measurements of the magnetic susceptibility in the paramagnetic region had indicated significantly larger values for the atomic magnetic moments than that measured for the ferromagnetic state; moreover, the value of the paramagnetic moment in the high-temperature gamma phase appeared to be much larger than that in the alpha-phase region. This anomalous behavior had been considered of sufficient significance that several theories had been advanced to account for these properties. There had also been some indications that gamma-iron might be antiferromagnetic. The neutron scattering measurements were taken at a series of temperatures up to about 1000°C, and there was no evidence for antiferromagnetic order in gamma-iron; moreover, the paramagnetic scattering suggested equivalent magnetic moments in the two phases with a value within 25% of the ferromagnetic moment. A very interesting feature of these measurements was the extremely intense critical magnetic scattering that developed at small angles in the temperature region near the Curie transition. This scattering was carefully investigated, and the results were analyzed [44] according to a formulation by Van Hove [47], which interpreted critical magnetic scattering

in terms of fluctuations in magnetic moment density and range of correlations between spins. This analysis gave values of the correlation range that rapidly increased as the temperature approached the Curie point, and the correlation functions that were obtained showed consistency with measured values of the paramagnetic susceptibility.

7. Conclusion

The early work in neutron scattering at the Oak Ridge National Laboratory laid the foundation on which many neutron scattering programs have been built throughout the world. There is little doubt that between 1946 and 1950 nearly all of the advances in this field of research were made by Shull, Wollan, and their associates at Oak Ridge; after that period new programs were initiated in several laboratories, and the credits became more diffuse. The importance of neutron scattering was recognized relatively quickly; in fact, it was for his early work, and particularly for his investigations of magnetic phenomena, that Professor Shull was awarded the Oliver E. Buckley Solid State Physics Prize by the American Physical Society in 1956. However, it is certainly doubtful that anyone could have predicted the tremendous success that neutron scattering has enjoyed. Almost forty years after the initial experiments, it is still an extremely important and active area of research. The techniques have reached a degree of sophistication that were not even a dream in the early days, and the research has impacted nearly every branch of physical science.

The present neutron scattering research is still filled with exciting new discoveries, and these will undoubtedly continue for many years. However, there has certainly been no more exciting period than the early days at Oak Ridge. I was very fortunate to have become a part of that program in 1950. Dr. Wallace Koehler was even more fortunate; he preceded me in the program by

about a year. Both of us want to state emphatically that it was a wonderful way to begin a scientific career.

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Figure Captions

- Fig. 1. Photograph of first two-axis diffractometer used for neutron diffraction experiments at ORNL.
- Fig. 2. Photograph of first two-axis diffractometer built specifically for neutron diffraction research with E. O. Wollan and C. G. Shull in attendance.
- Fig. 3. First neutron powder diffraction pattern taken with polycrystalline NaCl.
- Fig. 4. First neutron Laue pattern taken for NaCl.
- Fig. 5. Portions of neutron powder diffraction patterns for isotopically enriched samples of NiO.
- Fig. 6. Schematic representation of four models proposed for the structure of ice.
- Fig. 7. Paramagnetic diffuse scattering of neutrons by polycrystalline salts containing Mn^{2+} ions.
- Fig. 8. Neutron diffraction patterns from polycrystalline MnO at temperatures above and below the Néel temperature of 122 K.
- Fig. 9. Intensity variation of the (111) Fe_3O_4 neutron powder diffraction reflection with different directions of magnetization.
- Fig. 10. Neutron powder diffraction patterns for α -Mn taken at 20 K and room temperature.

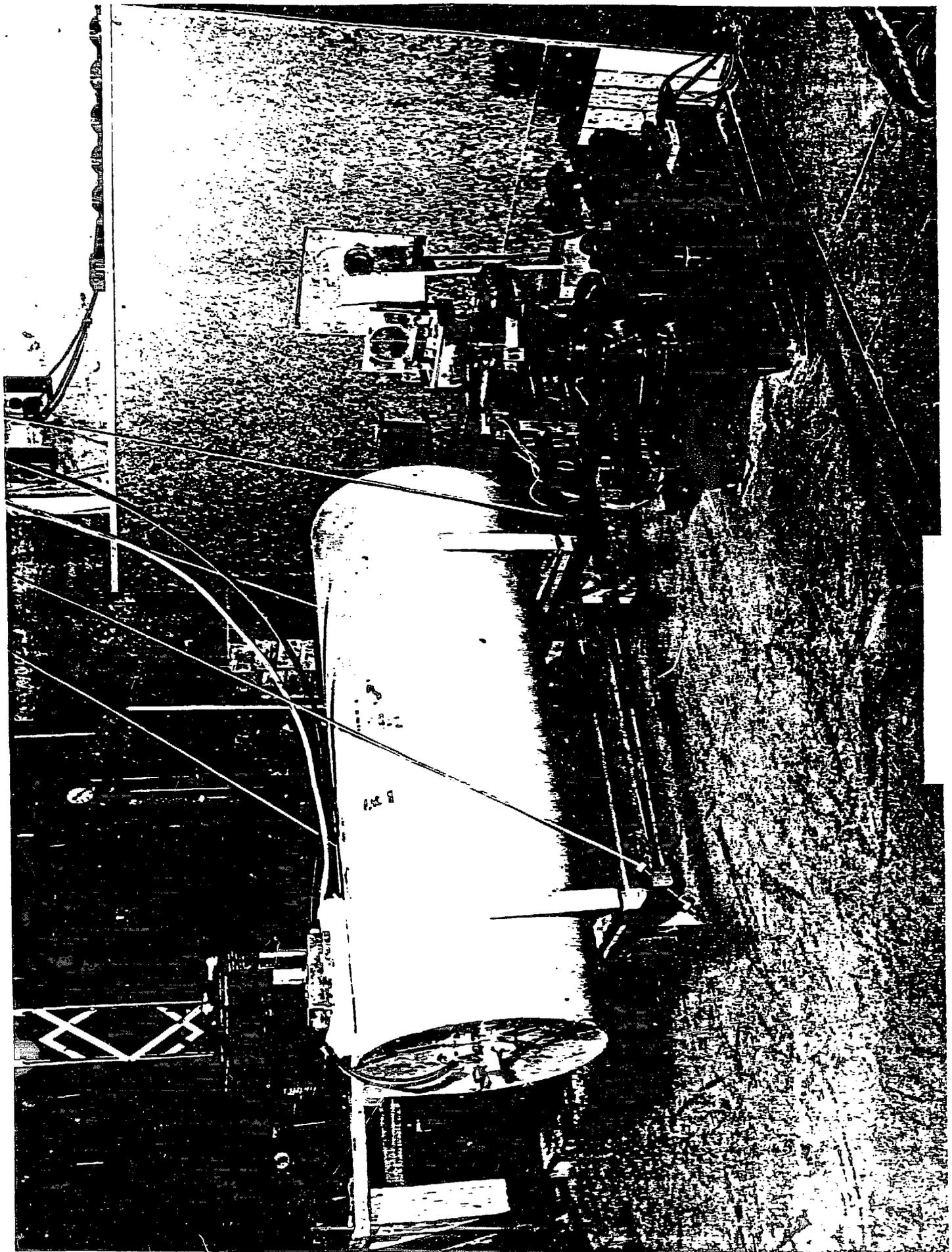


FIGURE 1

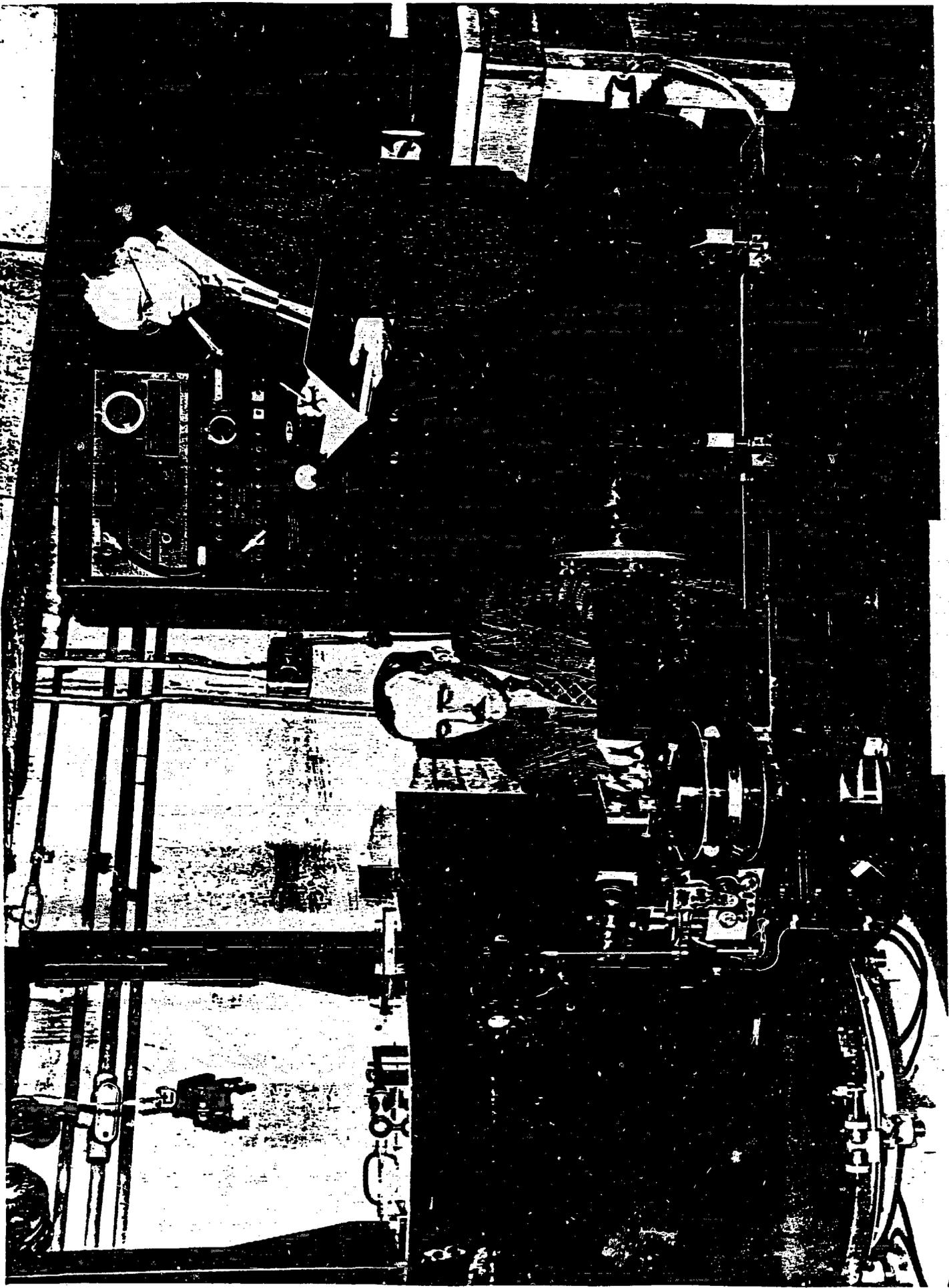


FIGURE 2

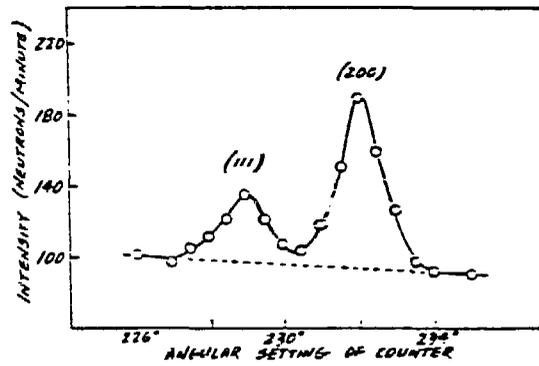


FIGURE 3



FIGURE 4

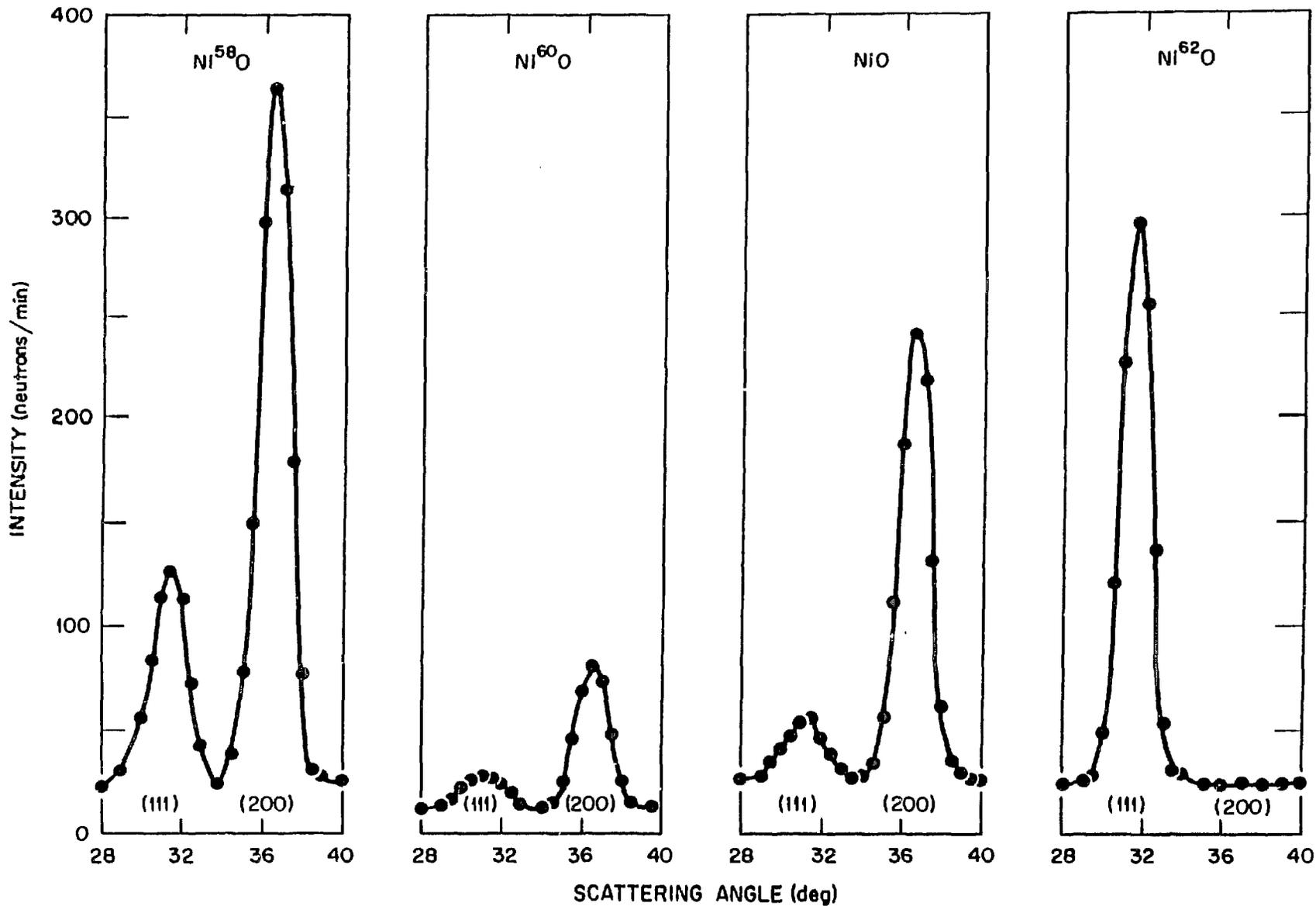
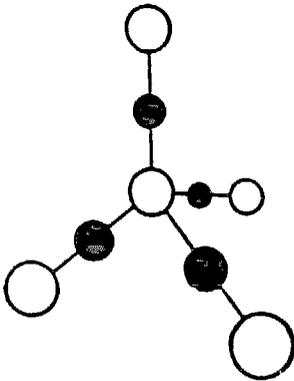


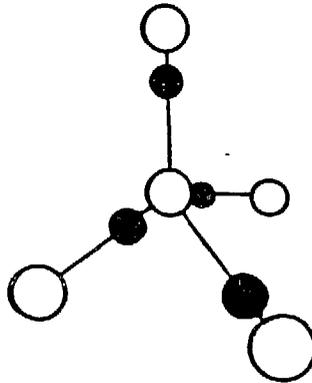
FIGURE 5

○ OXYGEN

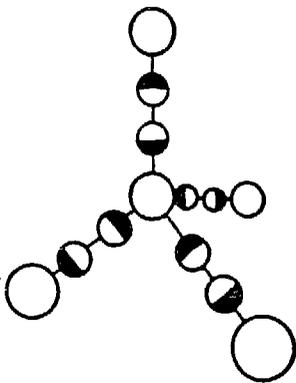
● HYDROGEN



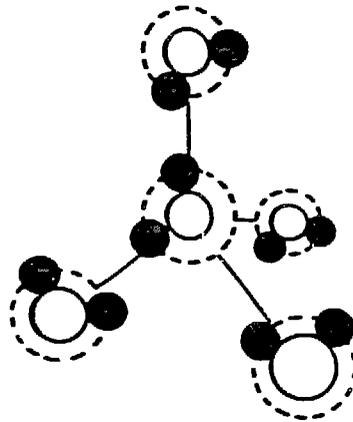
(A) BARNES



(B) BERNAL - FOWLER



(C) HALF - HYDROGEN



(D) HYDROGEN SHELL

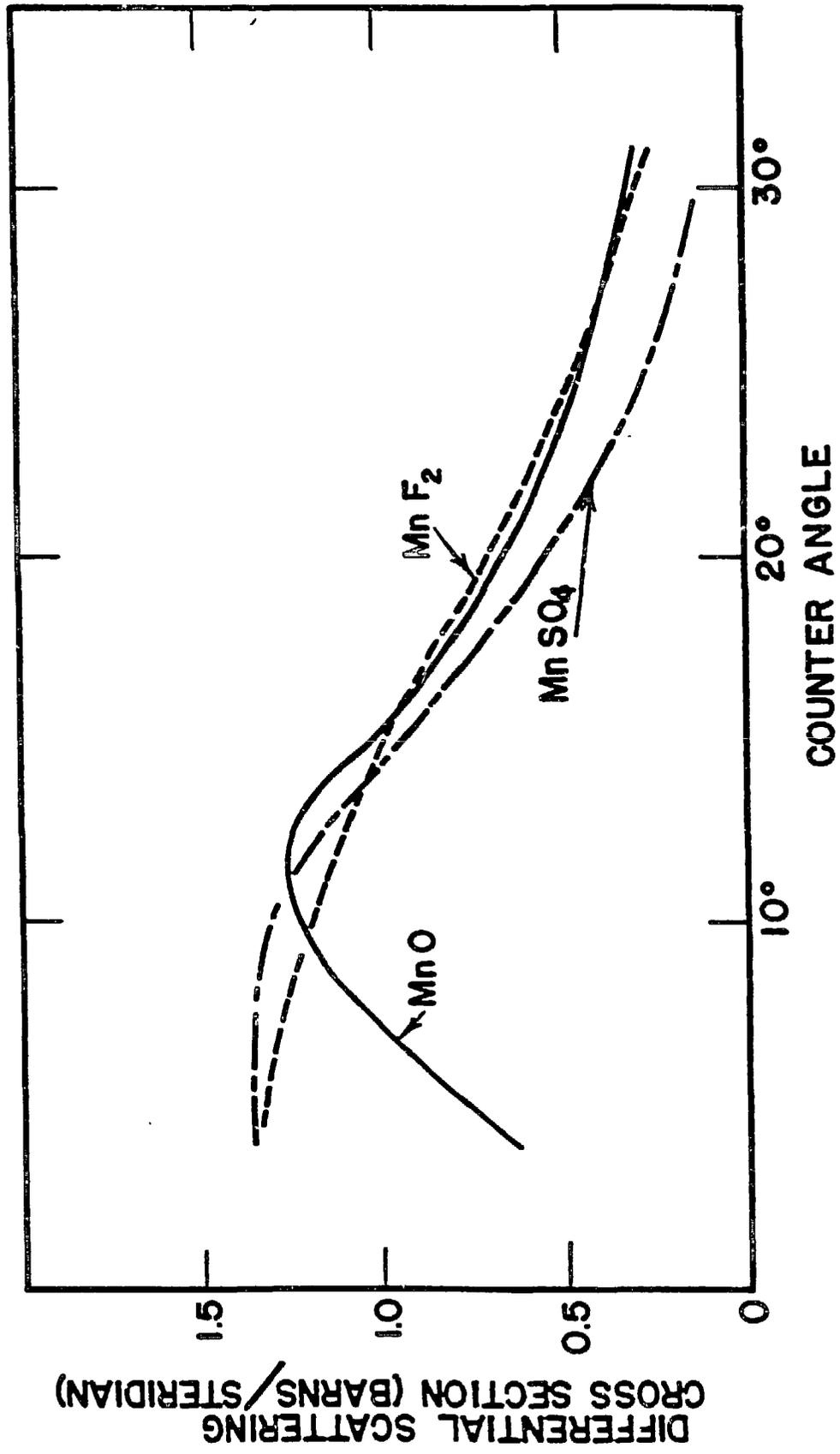
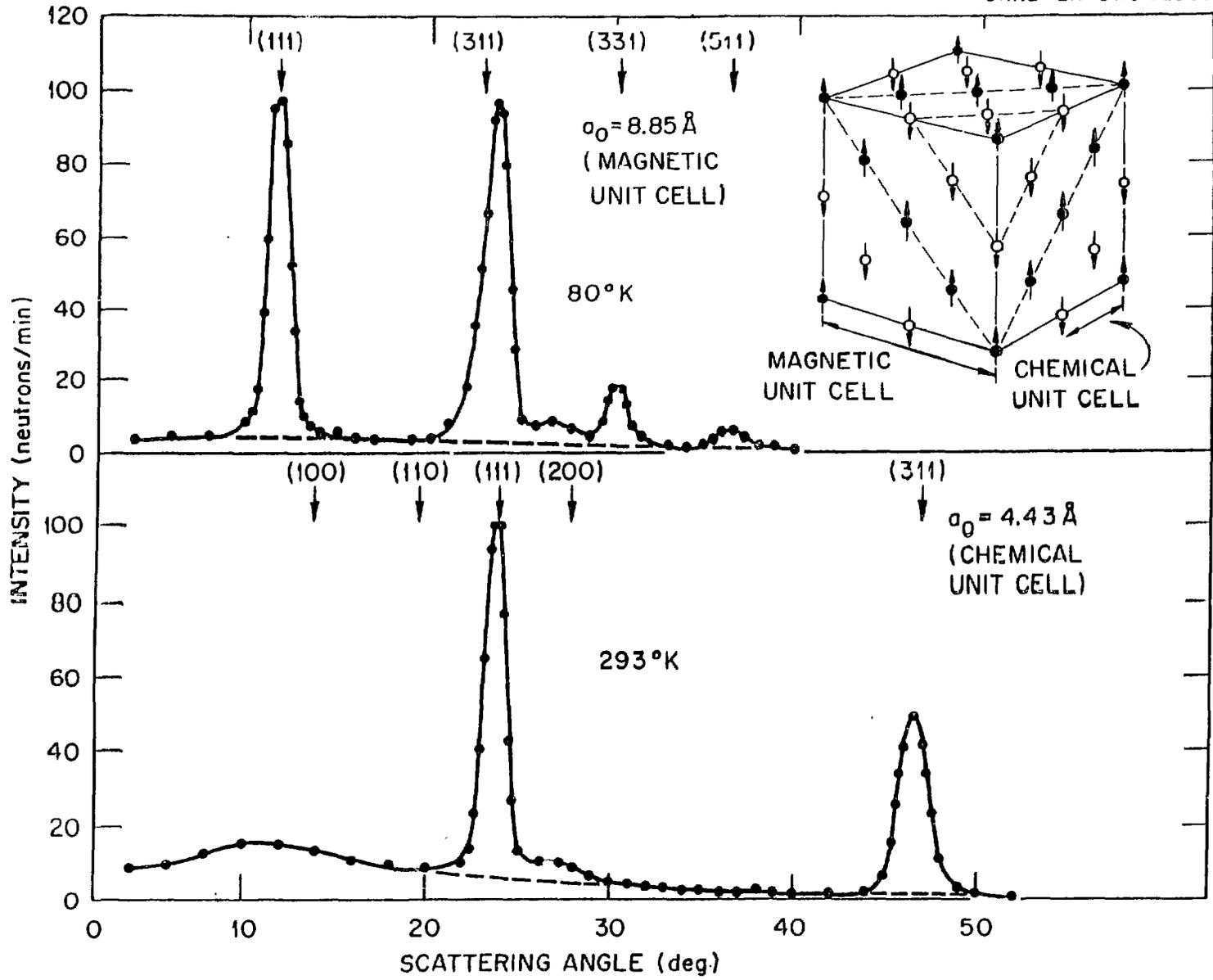


FIGURE 7



Powder Diffraction Patterns from MnO ($T_N = 122^\circ \text{K}$)

FIGURE 8

(III) Fe_3O_4 MAGNETIC REFLECTION

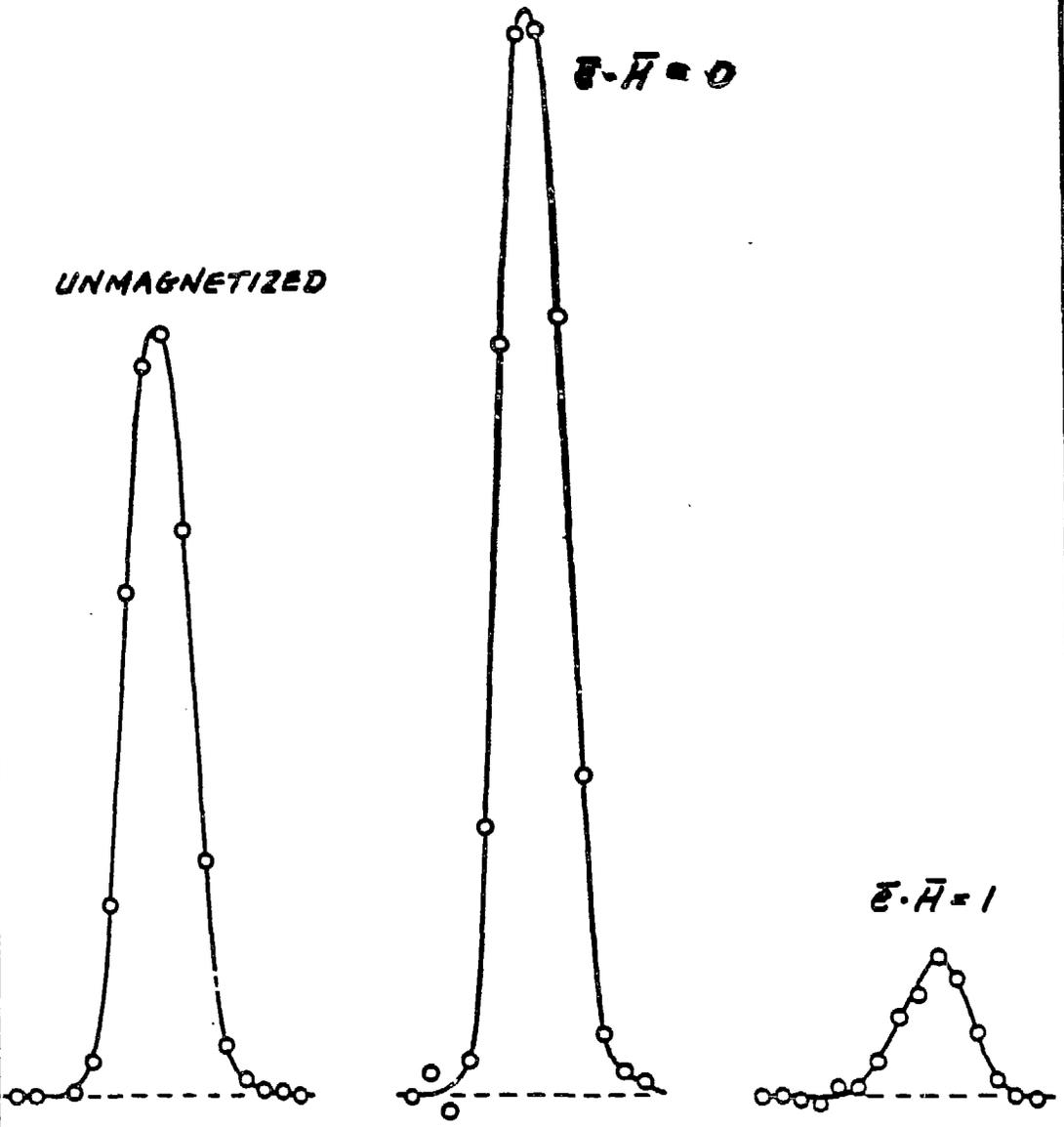


FIGURE 9

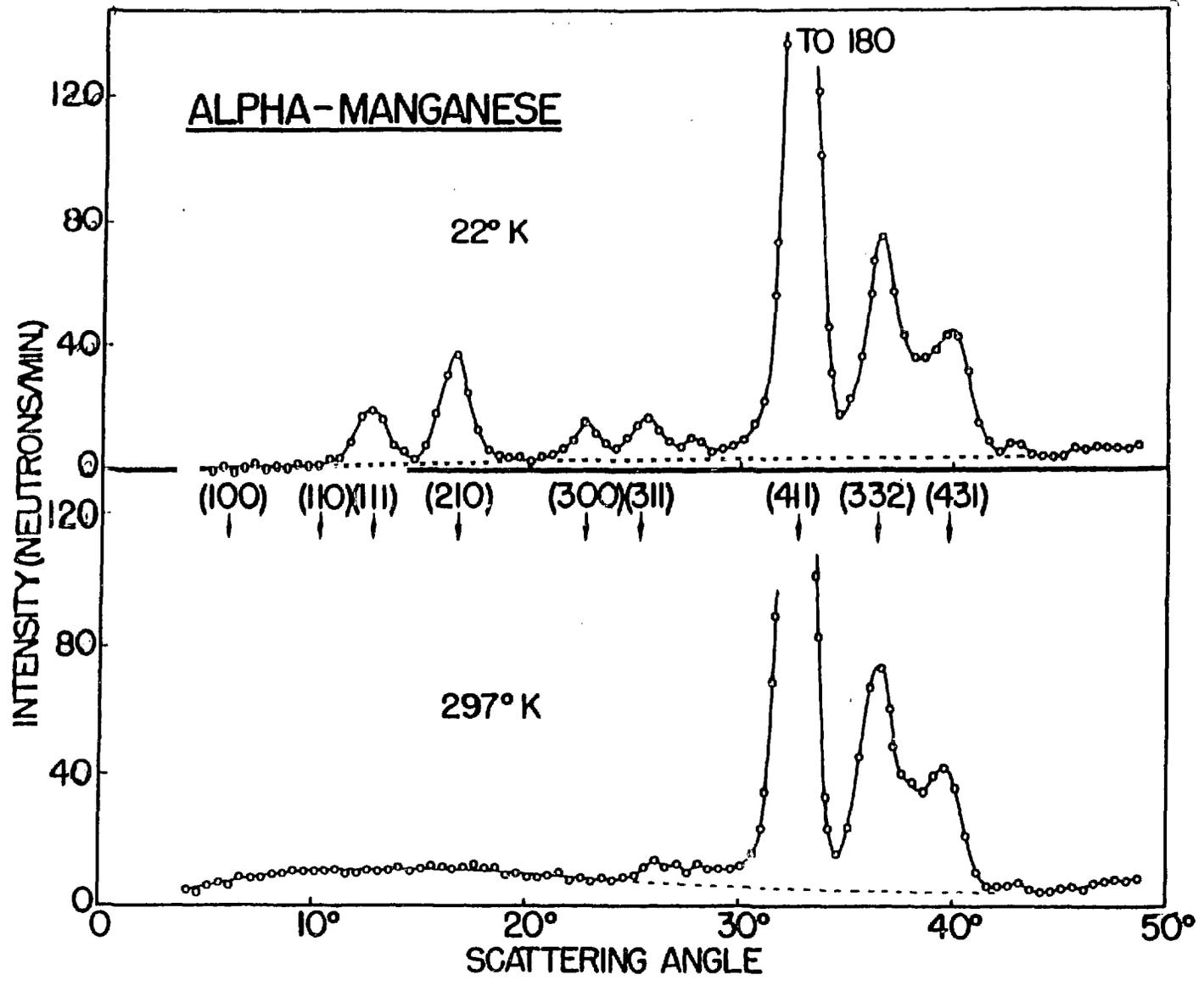


FIGURE 10