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Volume 23 PART A

Neutron Scattering

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PREFACE

The neutron scattering technique for measuring the structure and dynamics of condensed matter has developed over the 50 years of the neutron's history into a widely used tool in physics, chemistry, biology, and materials science. Since the early diffraction studies in the 1940s and the first measurements of inelastic scattering in the 1950s, developments in experimental methods have greatly increased the sensitivity and range of applications of the technique. Thus, while the early measurements probed distances on the order of interatomic spacings (~3 Å) and times on the order of typical periods of lattice vibrations (~1 ps), the current range of neutron scattering experiments covers distances from 0.1 to 10,000 Å, and times from 10 fs to 1 μs. This has been achieved by expanding the range of neutron energies available to the experimenter from a few milli-electron-volts (at cold sources in research reactors) to several electron-volts (at pulsed spallation sources), and by using a variety of novel detection methods such as position-sensitive detectors and back-scattering and spin-echo techniques. As a result, the areas of investigation have expanded from the conventional crystal structures and lattice dynamics (and their magnetic analogs) of 30 years ago to high-resolution studies of the atomic spacings in amorphous thin films, biological structures on a cellular scale, unraveling of long chains of polymers, and transitions between energy levels in molecular solids.

Along with these developments, the community of neutron users has expanded and diversified. Whereas 30 years ago neutron scattering was practiced largely by solid-state physicists and crystallographers, the users of present-day centralized neutron facilities include chemists, biologists, ceramicists, and metallurgists, as well as physicists of diverse interests ranging from fundamental quantum mechanics to fractals and phase transitions. The neutron centers have developed from essentially in-house facilities at the national nuclear research laboratories into centralized facilities organized for use by the general scientific community at an international level. The pioneer of this mode of operation was the Institut Laue-Langevin in Grenoble, France, operated since 1972 by Britain, France, and Germany as a user-oriented facility for scientists from these and other countries. Similar modes of operation are now being established at other major reactor facilities like those at Brookhaven and Oak Ridge in the United States, and the pulsed spallation sources that have recently come into operation at Argonne in the United States, the KEK Laboratory in Japan, and the Rutherford Laboratory in Britain have been set up from the beginning with this mode of operation. The current population of users of these and other neutron facilities has been recently estimated* to be 500 in the United States, 1250 in Western Europe, and about 200 in Japan.

The aim of the present book is to describe the current state of the art of application of neutron scattering techniques in those scientific areas that are most active. The presentation is aimed primarily at professionals in different scientific disciplines, from graduate students to research scientists and university faculty members, who may be insufficiently aware of the range of opportunities provided by the neutron technique in their area of specialty. It does not present a systematic development of the theory, which may be found in excellent textbooks such as those of Lovesey or Squires, or a detailed hands-on manual of experimental methods, which in our opinion is best obtained directly from experienced practioners at the neutron centers. It is rather our hope that this book will enable researchers in a particular area to identify aspects of their work in which the neutron scattering technique might contribute, conceive the important experiments to be done, assess what is required to carry them out, write a successful proposal for this purpose for one of the centralized user facilities, and carry out the experiments under the care and guidance of the appropriate instrument scientist. With this object in view, each chapter relating to a particular field of science has been written by a leading practitioner or practitioners of the application of the neutron methods in that field.

Volume 23, Part A, of this work starts out with a brief survey of the theoretical concepts of the technique and establishes the notation that will be used throughout the book. Chapters 2 and 3 review the fundamental hardware of neutron scattering, namely, sources and experimental methods, and Chapter 4 discusses fundamental physics applications in neutron optics. The remaining chapters of Part A treat various basic applications of neutron scattering to studies of the atomic structure and dynamics of materials. The Appendix contains a compilation of neutron scattering lengths and cross sections that are important in nearly all neutron scattering experiments.

Volume 23, Part B, contains surveys of the application of neutron scattering techniques to nonideal solids, such as solids with defects, two-dimensional solids and glasses, and to various classes of fluids. Finally, Volume 23, Part C, treats neutron scattering investigations of magnetic materials, solids undergoing phase transitions, and macromolecular and biological structures. In recognition of the expanding use of neutron scattering in technol-

* Current Status of Neutron-Scattering Research and Facilities in the United States (National Academy Press, Washington, D.C., 1984).

ogy, the last chapter in Part C is devoted to a survey of industrial applications.

We wish to thank the authors for taking time out of their busy schedules for contributing these chapters, Dr. R. Celotta for inviting us to undertake this work, and the staff of Academic Press for their encouragement and forbearance.

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LIST OF SYMBOLS

b	Bound scattering length
$\bar{b}$	Coherent scattering length
b^+	Scattering length for $I + \frac{1}{2}$ state
b^-	Scattering length for $I - \frac{1}{2}$ state
b_i	Incoherent scattering length
b_N	Spin-dependent scattering length
c	Velocity of light $= 2.9979 \times 10^{10}$ cm sec^{-1}
d	Mass density
$\mathbf{d}$	Equilibrium position of atom in unit cell
$\mathbf{D}_\perp(\mathbf{Q})$	Magnetic interaction operator
$d\sigma/d\Omega$	Differential cross section
$d^2\sigma/d\Omega\, dE$	Double differential cross section
E_0, E_1	Incident, scattered energy
E	Energy lost by neutron $(E_0 - E_1)$
e	Charge on the electron $= 4.8033 \times 10^{-11}$ esu
$\mathbf{e}^j(\mathbf{q})$	Polarization vector of normal mode j [$\mathbf{e}^j_d(\mathbf{q})$ for non-Bravais crystal]
$F(\boldsymbol{\tau})$	Structure factor for unit cell
$f(\mathbf{Q})$	Form factor
$G(\mathbf{r}, t)$	Space–time correlation function $[G_d(\mathbf{r}, t) + G_s(\mathbf{r}, t)]$
$G_d(\mathbf{r}, t)$	"Distinct" space–time correlation function
$G_s(\mathbf{r}, t)$	"Self" space–time correlation function
$g(\mathbf{r})$	Pair distribution function $[\rho(\mathbf{r})/\rho_0]$
$\hbar$	Planck's constant/2π $= 1.0546 \times 10^{-27}$ erg sec
$I(\mathbf{Q}, t)$	Intermediate scattering function $[I_d(\mathbf{Q}, t) + I_s(\mathbf{Q}, t)]$
$I_d(\mathbf{Q}, t)$	Intermediate "distinct" scattering function
$I_s(\mathbf{Q}, t)$	Intermediate "self" scattering function
$\mathbf{I}$	Angular momentum operator for nucleus
$\mathbf{k}_0$, $\mathbf{k}_1$	Incident, scattered wave vector
k_B	Boltzmann's constant $= 1.3807 \times 10^{-16}$ erg K^{-1}
$\mathbf{l}$	Position of unit cell
M	Mass of atom
m	Mass of neutron $= 1.0087$ u
m_e	Mass of electron $= 9.1095 \times 10^{-28}$ g
N	Number of unit cells in crystal
N_A	Avagadro's number $= 6.0220 \times 10^{23}$
$n(r)$	Radial distribution function $[4\pi r^2 \rho(\mathbf{r})]$
$\mathbf{Q}$	Scattering vector $(\mathbf{k}_0 - \mathbf{k}_1)$
$\mathbf{q}$	Reduced wave vector $(\mathbf{Q} - \boldsymbol{\tau})$
r	Number of atoms in a unit cell
r_0	Classical electron radius $(e^2/m_e c^2) = 2.8179 \times 10^{-13}$ cm
$\mathbf{S}$	Spin operator for ion or atom
$S(\mathbf{Q})$	Static structure factor $I(\mathbf{Q}, 0)$
$S_c(\mathbf{Q}, \omega)$	Coherent scattering function
$S_i(\mathbf{Q}, \omega)$	Incoherent scattering function
$\mathbf{s}$	Spin operator for electron

$\mathbf{u}$	Atomic mass unit = 1.6606×10^{-24} g
$\mathbf{u}^l$	Vibrational amplitude ($\mathbf{u}_d^l$ for non-Bravais crystal)
V	Volume of sample
v_0	Volume of unit cell
$2W$	Exponent of Debye–Waller factor (in cross section)
$Z(\omega)$	Density of phonon states
γ	Gyromagnetic ratio of neutron = 1.9132
Θ	Debye temperature
θ	Bragg angle
$\boldsymbol{\mu}$	Magnetic moment of ion or atom
μ_N	Nuclear magneton $(e\hbar/2m_pc) = 5.0508 \times 10^{-24}$ erg G^{-1}
μ_B	Bohr magneton $(e\hbar/2m_ec) = 9.2741 \times 10^{-21}$ erg G^{-1}
ρ_0	Average number density
$\rho(\mathbf{r})$	Pair density function $[G(\mathbf{r}, 0) - \delta(\mathbf{r})]$
σ	Bound total cross section (scattering plus absorption)
σ_c	Bound coherent scattering cross section
σ_i	Bound incoherent scattering cross section
σ_s	Bound scattering cross section $(\sigma_c + \sigma_i)$
$\frac{1}{2}\boldsymbol{\sigma}$	Spin operator for neutron
$\boldsymbol{\tau}$	Reciprocal lattice vector $\{2\pi[(h/a), (k/b), (l/c)]\}$
Φ	Neutron flux (n cm^{-2} sec^{-1})
ϕ	Scattering angle (= 2θ for Bragg reflection)
χ	Susceptibility
$\chi(\mathbf{Q}, \omega)$	Generalized susceptibility
Ω	Solid angle
$\omega_j(\mathbf{q})$	Frequency of normal mode j

CONTENTS

1. INTRODUCTION TO NEUTRON SCATTERING*

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1.1. General Principles of Neutron Scattering

1.1.1. Basic Properties of the Neutron

The neutron is a subatomic particle with zero charge, mass $m = 1.0087$ atomic mass units, spin $\frac{1}{2}$, and magnetic moment $\mu_n = -1.9132$ nuclear magnetons. These four properties combine to make the neutron a highly effective probe of condensed matter. The zero charge means that its interactions with matter are confined to the short-ranged nuclear and magnetic interactions, which in turn has two important consequences: the interaction probability is small, so the neutron can usually penetrate into the bulk of a sample of condensed matter and, as we shall see, it can be described in terms of the first Born approximation and thus given in explicit form by quite simple formulas.

Thermal neutrons for condensed matter research are usually obtained by slowing down energetic neutrons, produced by some type of nuclear reaction, by means of inelastic collisions in a moderating material containing light atoms. Most of the slow neutrons thus produced will have kinetic energies on the order of $k_B T$ where T is the moderator temperature, typically about 300 K, and k_B is Boltzmann's constant. If one considers the wave nature of the neutron, it can be described by a wavelength λ given by

$$h^2/2m\lambda^2 = k_B T, \tag{1.1}$$

* This work supported by the U. S. Department of Energy.

where h is Planck's constant. The value of the neutron mass is such that for $T \approx 300$ K and $\lambda \approx 2$ Å (2×10^{-8} cm), a distance comparable to the mean atomic separation in a solid or dense fluid. Such neutrons are therefore ideally suited to studies of the *atomic structure* of condensed matter in diffraction studies, a fact that was recognized soon after the neutron's discovery in 1932. Furthermore, the kinetic energy of such neutrons is on the order of 25 meV, which is a typical energy for collective excitations in solids and liquids. Thus, both wavelength and energy are ideally suited to studies of the *atomic dynamics* of condensed matter in inelastic scattering experiments—

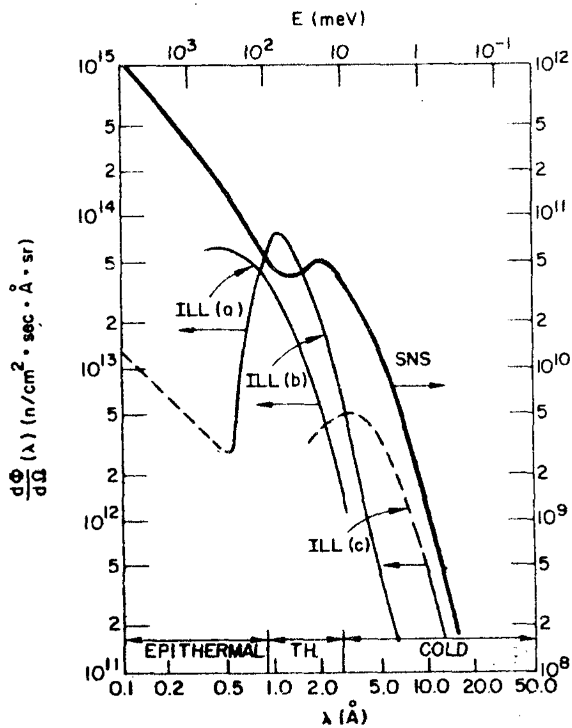

FIG. 1. Wavelength-dependent neutron spectra from (a) 2000 K graphite, (b) 300 K D_2O, and (c) 25 K liquid D_2 moderators at the Institut Laue-Langevin (ILL) high-flux reactor, and from a 25 K liquid H_2 moderator at the Rutherford-Appleton Laboratory spallation neutron source (ISIS). Preliminary SNS data (time-averaged fluxes) have been scaled to design proton current of 200 μA and moderator area of 100 cm^2. The scale for SNS values (right-hand scale) has been shifted up by factor 10^3 to roughly represent the increased efficiency for time-of-flight experiments due to the pulse structure. [ILL data from manual "ILL Neutron Beam Facilities" (1974); SNS data from T. G. Perring *et al.*, *Rutherford Appleton Lab. Rep.* **RAL-85-029** (1985).]

experiments in which simultaneous transfer of momentum and energy is observed.

The magnetic moment of the neutron makes it a unique probe of *magnetism* on an atomic scale: neutrons may be scattered from the magnetic moments associated with unpaired electron spins in magnetic samples. Again, the wavelength and the energy of a thermal neutron are such that both the magnetic structure and the dynamics of the spin system can be studied in the neutron scattering experiment.

The spin of the neutron has further important consequences: when a neutron is scattered by a nucleus with nonzero spin, the strength of the interaction depends on the relative orientation of neutron and nuclear spins. This makes the neutron a unique probe of *nuclear spin correlation and ordering* at low temperatures.

Figure 1 shows typical energy spectra of neutrons produced by two common types of source: a nuclear reactor and a pulsed spallation source (details of these and other sources are given in Chapter 2). It is conventional to categorize neutrons by the moderator temperature—cold, thermal, or hot—that they would be in equilibrium with; neutrons that have not yet slowed down to equilibrium velocities are called epithermal. The approximate regions for the different categories are indicated in Fig. 1, and in Table I the energy, temperature, wavelength, wave vector, and velocity are given for typical neutrons in each category.

In subsequent chapters we discuss different kinds of atomic and molecular excitations in condensed matter. Various ways of denoting the energies of these excitations are in use: Table II gives a conversion table between the more common units.

TABLE I. Characteristics of Neutrons at Selected Energies

Quantity	Unit	Definition	Ultracold	Cold	Thermal	Epithermal
Energy E	meV[a]		0.00025	1	25	1000
Temperature T	K	E/k_B	0.0029	12	290	12,000
Wavelength λ[b]	Å	$h/(2mE)^{1/2}$	570	9.0	1.8	0.29
Wave vector $\mathbf{k}$[c]	$Å^{-1}$	$(2mE)^{1/2}/h$	0.011	0.7	3.5	22
Velocity v[d]	m/s	$(2E/m)^{1/2}$	6.9	440	2200	14,000

[a] 1 meV = 1.6022×10^{-15} erg, the energy required to raise a proton up to a potential of 1 mV.
[b] λ (Å) = 9.0446 [E (meV)]$^{-1/2}$.
[c] k ($Å^{-1}$) = 0.69469 [E (meV)]$^{1/2}$.
[d] v (m/s) = 437.39 [E (meV)]$^{1/2}$.
Source: "CRC Handbook of Chemistry and Physics" (R. C. Weast, M. J. Astle, and W. H. Beyer, eds.), 65th ed., CRC Press, Boca Raton, Florida, 1984.

TABLE II. Quantities Used to Denote Neutron Energy

Quantity	Definition	Value at $E = 1$ meV
Angular frequency ω	$E/\hbar$	1.5193×10^{12} rad/s
Frequency ν	E/h	0.24180 THz
Wave number $\tilde{\nu}$	E/hc	8.0655 cm^{-1}
Temperature T	E/k_B	11.605 K

Source: "CRC Handbook of Chemistry and Physics" (R. C. Weast, M. J. Astle, and W. H. Beyer, eds.), 65th ed., CRC Press, Boca Raton, Florida, 1984. h is Planck's constant, $\hbar = h/2\pi$ and c is the velocity of light.

1.1.2. Interactions between Slow Neutrons and Condensed Matter

We consider a simple scattering experiment schematically shown in Fig. 2. Suppose that a beam of neutrons characterized by a wave vector $\mathbf{k}_0$ falls on the sample. As pointed out in the previous section, the interaction probability is rather small and in a typical experimental situation most neutrons are transmitted without any interaction. Some, however, will be scattered and can be measured with a neutron detector placed, let us say, in direction $\hat{\mathbf{k}}_1$. If the incident beam is characterized by a uniform flux Φ (neutrons crossing unit area per unit time), the sample has N identical atoms in the beam, and the detector subtends a solid angle $\Delta\Omega$ and has efficiency η, we may expect the count rate C in the detector to be proportional (if $\Delta\Omega$ is small enough) to all these quantitites. This is indeed the case, and the constant of proportionality is called the *differential cross section* and is defined by

$$\frac{d\sigma}{d\Omega} = \frac{C}{\Phi N(\Delta\Omega)\eta}. \tag{1.2}$$

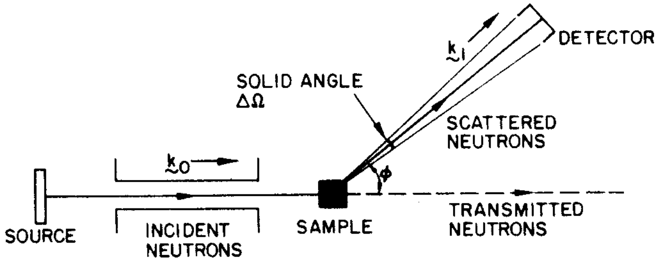

FIG. 2. Schematic diagram of a neutron scattering experiment. [Note: On this figure and throughout chapter, an undertilde denotes a vector.]

The differential cross section is a function of the magnitude and direction of $\mathbf{k}_0$ and the direction of $\hat{\mathbf{k}}_1$ and is a property of the sample being measured; it may also depend on the spin state of the incident neutron.

The most important types of interaction for condensed matter studies are the nuclear interaction and the magnetic dipole interaction. Other, much weaker, interactions are discussed by Shull[1].

1.1.2.1. Nuclear Scattering. The interaction between a slow neutron* and an atom through the nuclear force can be expressed in a very simple form. To illustrate this we consider the case where the atoms in the sample are both noninteracting and identical. In this case the differential cross section is just a constant:

$$\frac{d\sigma}{d\Omega} = b^2 \tag{1.3}$$

where the scattering length b is a property only of the nucleus of the scattering atom (its atomic number Z and atomic weight A) and, in general, its spin state relative to that of the neutron.

The scattering length is a quantity that depends on the details of the interaction between the neutron and the components of the nucleus. For this reason both the sign and magnitude of b change in an irregular fashion with Z and A, in contrast to x-ray scattering for which the atomic scattering length is a monotonically increasing function of Z. This is illustrated in Fig. 3.

This fact has some powerful consequences, making neutrons sensitive to the presence of light atoms, notably hydrogen, and to the difference between atoms with similar atomic number, for example, adjacent transition metals. The variation in scattering length between different isotopes of the same element is often large and can be exploited in experiments using isotope substitution.

In many cases the scattering lengths for the two spin states, $I \pm \frac{1}{2}$, of the neutron-nucleus system are also quite different, which, in general, leads to "incoherent" scattering as discussed in Section 1.2. If the nuclei are polarized, the spin dependence of the scattering length can be exploited to measure the configuration of the nuclear spins (Section 1.8).

In some cases the scattering length is complex. This situation arises when there is a low-lying resonance of the neutron–nucleus system, leading to scattering and absorption cross sections that depend on wavelength; the values for $\lambda = 1$ Å are shown in Fig. 3 in this case.

Finally, we point out that the scattering intensity in the simple case discussed previously will depend on whether the nuclei are fixed or free to

* For this discussion we require that the neutron wavelength be much greater than the range of the nuclear force, a condition clearly satisfied for the neutrons of interest here.

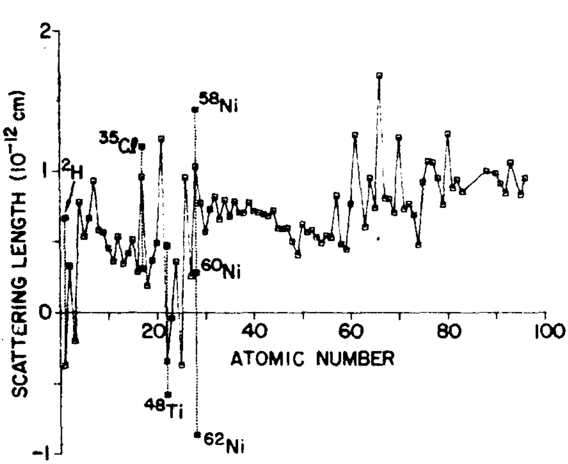

FIG. 3. Values of the bound-atom scattering length for the different elements. Values are shown for naturally abundant isotopic compositions. The solid squares indicate some values for separated isotopes often used in isotope-substitution experiments.

recoil in the scattering process: the scattering length measured in the laboratory system is smaller by a factor $(A/A + 1)$ if the nucleus is free to recoil. For most condensed-matter neutron scattering experiments, the fixed atom is a more appropriate limiting case, and it is conventional to quote the corresponding "bound-atom" values for scattering lengths and cross sections. We will return to the free-atom case in discussing scattering from the ideal gas (Section 1.4.5).

A list of scattering lengths with corresponding cross sections is given in the Appendix to this volume, which also includes a theoretical discussion and a description of methods of measuring these quantities.

1.1.2.2. Magnetic Scattering. The neutron has a magnetic moment, $\mu_n = -1.913$ nuclear magnetons, which can interact with the unpaired electrons in magnetic samples. We will consider the simple case of a paramagnet with electrons localized on specific ions with random spin orientations and no external magnetic field. The differential cross section is then given by the formula

$$\frac{d\sigma}{d\Omega} = (\gamma r_0)^2[f(\mathbf{k}_1 - \mathbf{k}_0)]^2 S(S + 1), \tag{1.4}$$

where $\gamma r_0 \approx 0.54 \times 10^{-12}$ cm, S is the spin quantum number for the ions, and $f(\mathbf{Q})$, the magnetic form factor, is given by the Fourier transform of the density distribution of the unpaired electrons about the ion center, normalized so that $f(0) = 1$. The form factor appears because the spatial distribution of magnetic electrons about the ion center is comparable to the interatomic spacing and thus to the wavelength of the neutrons used in the scattering experiment. This is in contrast to the short-range nuclear force with a Fourier transform that is effectively constant. Unlike the nuclear scattering length, however, the magnetic form factor can often be calculated quite accurately from the electronic wave functions. A typical case is shown for iron in Fig. 4. Conversely, measurements of the form factor with the use of Eq. (1.4) yield direct information about the wave functions of the magnetic electrons.

In addition to scattering from the spins, the magnetic moment of the neutron can interact with the current associated with a moving electron, and then there will be an orbital contribution to the magnetic interaction. In view of the more complicated form of the expressions for magnetic scattering, we develop the formalism of the next three sections in terms of the nuclear interaction, returning to the magnetic interaction in Sections 1.6 and 1.7.

1.1.2.3. Nuclear Absorption. At the beginning of this section we discussed two possible outcomes for a neutron incident on the sample: transmission and scattering. A third possibility is absorption by a nucleus, either through a direct nuclear reaction or as a result of compound nucleus formation. In most scattering experiments this can be treated as a simple attenuation of the incident and scattering beams in terms of a numerical factor that must be included in Eq. (1.2) along with other "non-ideal" factors

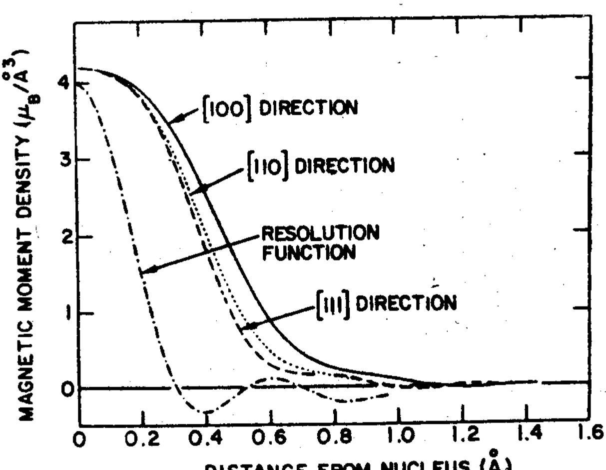

FIG. 4. Magnetic form factor for iron. [From Shull and Yamada[40].]