Total Neutron Cross Sections of Compounds with Different Crystalline Structures*

LESTER WINSBERG, DAVID MENEGHETTI, AND S. S. SIDHU**
Argonne National Laboratory, Chicago, Illinois
(Received November 22, 1948)

The total neutron cross sections of polycrystalline compounds, such as close-packed hexagonal ZnO, body-centered cubic TlBr, and face-centered cubic CaO and TiC were determined with the Argonne neutron velocity selector and neutron crystal spectrometer in the energy region of 0.001 to 1.0 electron volt. From the size of the cross-section peaks which are due to coherent scattering of neutrons the following scattering amplitudes were determined: Ca, $+0.46 \times 10^{-12}$ cm; Ti, -0.25×10^{-12} cm; Tl, $+0.75 \times 10^{-12}$ cm. The previously reported value of $+0.58 \times 10^{-12}$ cm for Zn was confirmed. The free atom scattering cross section of Ca is 2.5 barns.

INTERFERENCE effects are observed when photons or particles of appropriate wave-length impinge on crystalline matter. For diffraction to occur the wave-length of the impinging radiation must be less than twice the largest interplanar distance in the crystal but not smaller by too large an order of magnitude. The intensity of the scattered beam is usually measured as a function of the scattering angle and the wave-length of the impinging radiation. Since the intensity of the transmitted beam is decreased by the amount of scattered and absorbed radiation, diffraction effects may also be observed if transmission measurements are made as a function of the wave-length of the incident beam.

Halpern, Hamermesh, and Johnson,[1] and Weinstock[2] have theoretically determined the nature of the transmission curve as a function of wave-length for neutrons passing through a mono-atomic microcrystalline substance. Fermi, Sturm, and Sachs[3] extended this treatment to diatomic substances and determined the theoretical and experimental curves for Be and BeO. In the present investigation the method was applied to the study of crystalline and nuclear properties of some simple diatomic substances with body-centered and face-centered cubic, and hexagonal close-packed structures.

EXPERIMENTAL PROCEDURE AND RESULTS

The two devices used for velocity selection of neutrons from the Argonne heavy water pile were the rotating shutter mechanism designed by Brill and Lichtenberger[4] and the crystal spectrometer described by Zinn[5] and Sturm.[6] The rotating shutter mechanism employs the time of flight method for determining the energy of neutrons. Its operating range was 0.001 to 0.2 electron volt. The energy range of neutrons obtained by means of the crystal spectrometer was 0.1 to 1.0 electron volt.

The samples were in the form of powders ground to finer than 200 mesh and were contained in aluminum containers with inner end dimensions of $1\frac{1}{2}'' \times 4\frac{1}{2}''$ and lengths varying from 2″ to 10″, depending on the desired transmissions in the region of 0.25 to 0.5. In the case of samples with high absorption and low scattering of neutrons it was necessary to use a sample having low transmission in order to determine with sufficient accuracy the contribution of coherent scattering to the total cross section of the material.

The transmission T of the sample for neutrons of given velocity was determined from the ratio of the counting rates obtained with and without the sample in the path of the beam corrected for the fast neutron background. From the weight of the sample and the inner end area of the container the number N of formula molecules per unit end area was calculated. The cross section was then determined from

$$\sigma = (1/N) \ln(1/T). \tag{1}$$

The theoretical cross-section curves due to coherent scattering alone were calculated from the relation:[3]

$$\sigma = \sum_{n/d \leq 2/\lambda} \frac{FM\lambda^2 d}{g\sqrt{8}\pi n} \exp(-\omega(n/d)^2) \tag{2}$$

[1] O. Halpern, M. Hamermesh, and M. H. Johnson, Phys. Rev. **59**, 981 (1941).
[2] R. Weinstock, Phys. Rev. **65**, 1 (1944).
[3] E. Fermi, W. J. Sturm, and R. G. Sachs, Phys. Rev. **71**, 589 (1947).
[4] T. Brill and H. V. Lichtenberger, Phys. Rev. **72**, 585 (1947).
[5] W. H. Zinn, Phys. Rev. **71**, 752 (1947).
[6] W. J. Sturm, Phys. Rev. **71**, 757 (1947).

TABLE I. Structure factors and multiplicity factors of CaO, TiC, TlBr, and ZnO.

Element	Miller indices	M	$F/4\pi$	$FM/4\pi$ $\times 10^{-24}$ cm²
CaO	111	8		3
	311	24	$16(Ca-O)^2$	9
	331	24		9
	200	6		110
	220	12	$16(Ca+O)^2$	220
	222	8		146
TiC	111	8		109
	311	24	$16(Ti-C)^2$	326
	331	24		326
	200	6		17
	220	12	$16(Ti+C)^2$	34
	222	8		23
TlBr	100	6		0.2
	111	8	$(Tl-Br)^2$	0.3
	210	24		0.9
	110	12		20.6
	200	6	$(Tl+Br)^2$	10.3
	211	24		41.3
ZnO	100	6	$(Zn+O)^2$	8.5
	002	2	$4(Zn^2+O^2-0.070\ Zn\cdot O)$	5.5
	101	12	$3(Zn^2+O^2-1.39\ Zn\cdot O)$	7.8
	102	12	$(Zn^2+O^2-0.070\ Zn\cdot O)$	8.2
	110	6	$4(Zn+O)^2$	34.0
	103	12	$3(Zn^2+O^2+1.49\ Zn\cdot O)$	44.4
	200	6	$(Zn+O)^2$	8.5
	112	12	$4(Zn^2+O^2-0.070\ Zn\cdot O)$	32.8
	201	12	$3(Zn^2+O^2-1.39\ Zn\cdot O)$	7.8
	004	2	$4(Zn^2+O^2-1.995\ Zn\cdot O)$	0.02

in which the structure factor F of the lattice made up of diatomic substance was calculated as follows:

$$F=4\pi \left| A_1 \sum_{u_1v_1w_1} \exp[2\pi i(hu_1+kv_1+lw_1)] \right.$$
$$\left. +A_2 \sum_{u_2v_2w_2} \exp[2\pi i(hu_2+kv_2+lw_2)] \right|^2, \quad (3)$$

where A_1 and A_2 are the scattering amplitudes of atoms of species 1 and 2, u, v, and w are the coordinates of the atoms in the unit cell, and h, k, and l are the Miller indices. In expression (2) M is the multiplicity factor (the number of different orientations of the unit cell such that the Bragg condition for a given set of crystal planes is satisfied), λ the wave-length of the neutrons, V the volume of the unit cell, d the interplanar spacing for a given set of crystal planes, n the order of reflection, and g the number of molecules per unit cell. The exponential term is a Debye-Waller type correction factor for

thermal agitation, in which ω is a function of the Debye temperature.[2]

Where the scattering amplitudes were known, the coherent scattering cross section as a function of energy was calculated from Eqs. (2) and (3). The contribution due to absorption was calculated from the value of the absorption cross section at 0.025 electron volt[7] on the assumption that the absorption cross section varied inversely proportional to the neutron velocity. The sum of the two calculated cross sections was compared with the experimentally obtained values. Where the scattering amplitude was not known, its value was taken to be that which gave the best fit of the resultant curve above and below the position of the first appearance of diffraction effects.

It should be noted that for nth order diffraction from a given set of parallel planes the maximum cross section occurs at the wave-length $\lambda=2d/n$. The energy values corresponding to these wave-lengths are marked on all the figures given below. The coherent scattering cross section for neutrons of wave-length longer than $2d/n$ is zero for the given value of n and d.

A. CaO

An 8-inch long container was filled with 476.8 grams of chemically pure CaO which had been dried for several days at 950°C. The sample was kept in a desiccator at all times except during an
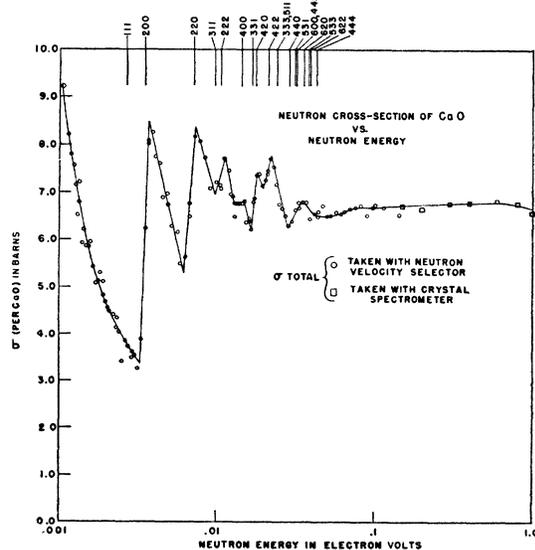

FIG. 1. Neutron cross section of CaO vs. neutron energy.

7 Project Handbook—CL—697, Chapter IVA, 3.1, p. 21.

actual cross-section measurement. These pre-
cautions were necessary to avoid absorption of
water.

The structure of calcium oxide is face-centered
cubic. Fermi and Marshall[7] give the scattering
amplitudes of Ca and O as 0.79 and 0.61, respec-
tively, in units of 10^{-12} cm. The signs of the
scattering amplitudes are both positive, i.e., the
change in the phase of the neutron wave on
scattering by Ca is the same as for O. As given
in Table I, the structure factors for diffractions
involving all odd indices are proportional to the
factor (Ca−O) where the chemical symbols rep-
resent the scattering amplitudes. For all even
indices the factors are proportional to (Ca+O).
This is confirmed by Fig. 1. The first two peaks
can be unambiguously assigned to diffraction
involving even indices (200) and (220). Further-
more, the (111) peak is either very weak or com-
pletely absent. The positions of the other peaks
are in accord with the assigned signs of the scat-
tering amplitudes, although the agreement in
these cases is not as definite. Because of the
limited resolution of the instrument, the cross-
section peaks obtained experimentally occur at
slightly higher energies than the calculated
values.

The calculated cross-section curve, based on
the data of Fermi and Marshall[8] and a value of
570°K for the Debye temperature determined
from the heat capacity data, is larger than the
experimental curve obtained here by a factor of
almost 2. The best fit of the experimental and
calculated curves was for a value of 0.46±0.05
for the scattering amplitude of Ca based on the
value of 0.61 for O. The free atom scattering
cross section of Ca can be calculated by the
formula $\sigma = 4\pi A^2\mu^2$, where A is the value of the
scattering amplitude and μ is the reduced mass
of a neutron and a free Ca atom. This formula is
strictly valid only for mono-isotopic elements but
is assumed accurate enough here within the un-
certainty in the scattering amplitude, since the
isotopic abundance of Ca^{40} is 97 percent, the
remainder being divided among 5 isotopes. The
free atom scattering cross section based on the
value of 4.1 barns for O was also determined
from the experimental curve at one electron
volt. The value obtained by both the rotating
shutter method and the crystal spectrometer was
2.5±0.3 barns. It is much less than any value
previously reported.

[8] E. Fermi and L. Marshall, Phys. Rev. 71, 666 (1947).
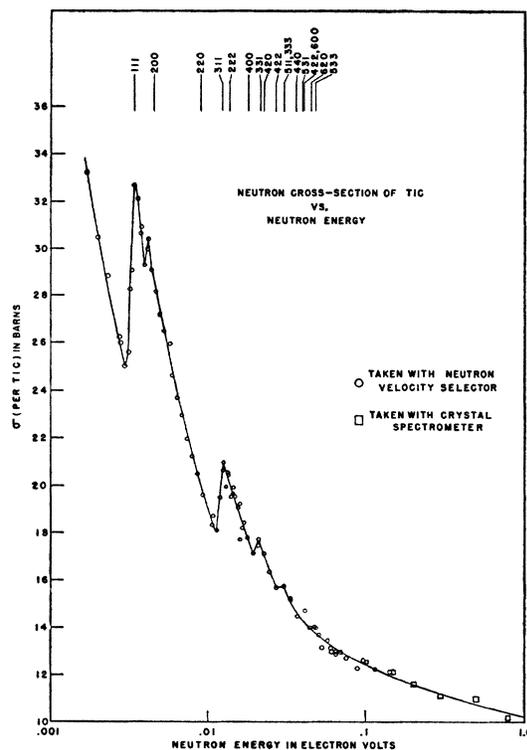

FIG. 2. Neutron cross section of TiC vs. neutron energy.

B. TiC

A 2-inch long container was filled with 378.2
grams of TiC. Since the compound has a low
avidity for water, further drying was unnecessary.

Like CaO, TiC crystallizes in a face-centered
cubic structure. While the scattering amplitude
of C is given as +0.67,[8] neither the sign nor the
magnitude of the scattering amplitude of Ti has
been known.

Whereas in the case of CaO the cross-section
values for diffractions involving even indices was
large and those involving odd indices very small,
the situation is reversed in the case of TiC. As
seen in Fig. 2, the intense peaks can be unam-
biguously assigned to diffractions from the (111)
and (311) planes. Possible peaks corresponding
to the (200) and (220) planes are relatively weak.
The change in the phase of the neutron on scat-
tering by Ti is, therefore, different by the angle
π from that for C, i.e., the sign of its scattering
amplitude is negative. The large continuous rise
of the curve with decreasing energy is due
primarily to the high 1/v absorption cross section
of titanium. The scattering amplitude was cal-
culated from the curve to be −0.25±0.03. The
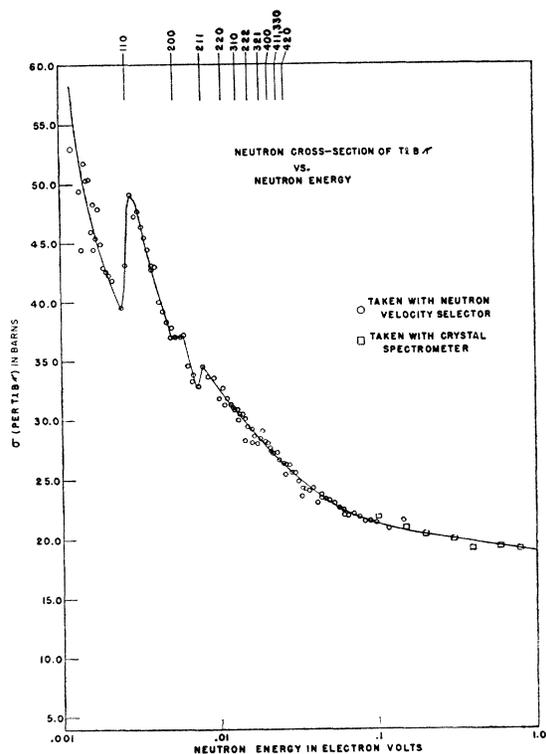Debye temperature was not known. Calculations

FIG. 3. Neutron cross section of TlBr vs. neutron energy.

were, therefore, made by assuming it to be 500°K, 1000°K, and 1500°K. The lowest value of the exponential term in Eq. (2) for the (111) planes was 0.96 for a Debye temperature of 500°K. Because the term decreases in magnitude for larger indices, the value of the scattering amplitude was calculated primarily from the (111) peak and is, therefore, relatively reliable. The structure factors for various crystalline planes of TiC, based on the above value of the scattering amplitude of Ti, and the multiplicity factors are given in Table I.

C. TlBr

A container similar to that used for TiC was filled with 887.5 g of TlBr which had been dried for 3 days at 400°C. The scattering amplitude of Br is given as +0.56,[8] and that of Tl is determined here.

The structure of TlBr is of the CsCl type, in which the cross-section values depend strongly on whether the sum of the Miller indices is even or odd. For scattering amplitudes with like sign, large cross-section peaks will occur at positions corresponding to indices of even sum. On the other hand, if the Tl and Br atoms scatter

neutrons out of phase the peaks corresponding to indices of odd sum would be prominent.

As shown in Fig. 3, the peaks in the cross-section curve occur at positions corresponding to an even sum of Miller indices. Thus, Tl and Br scatter in phase, i.e., the sign of the scattering amplitude of Tl is positive. From analysis of the curve the magnitude of the scattering amplitude was found to be 0.75 ± 0.08, based on the value of $+0.56$ for Br[8]. A Debye temperature $\sim500°K$, determined from heat capacity data, was used in the calculations. The structure and the multiplicity factors for this compound are also given in Table I.

D. ZnO

A 6-inch long container was filled with 873.7 grams of ZnO, which had been dried for several days at 900°C, and a total cross-section curve as a function of energy was obtained as shown in Fig. 4. Since this compound crystallized in a close-packed hexagonal structure with the following coordinates of the atoms in the unit cell, $Zn: 0, 0, 0; \frac{1}{3}, \frac{2}{3}, \frac{1}{2}, and O: 0, 0, \mu; \frac{1}{3}, \frac{2}{3}, (\frac{1}{2}+\mu)$, where $\mu = 0.3725$, its structure factor is given by the expression:
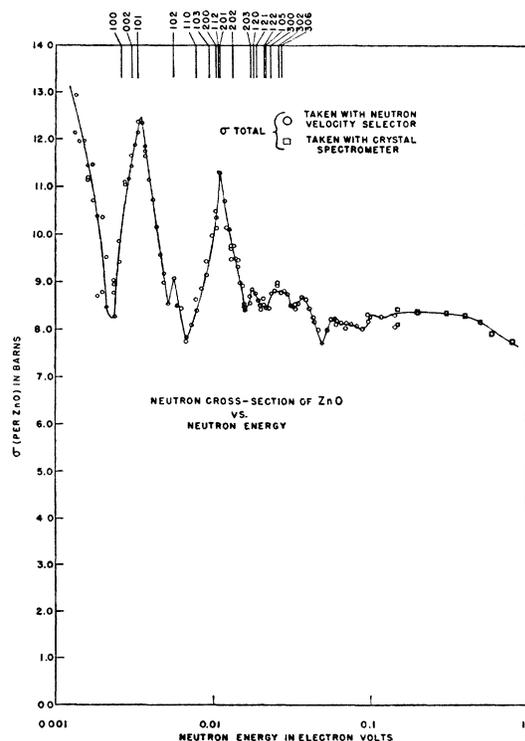

FIG. 4. Neutron cross section of ZnO vs. neutron energy.

$$F = 8\pi[1 + \cos2\pi(h/3 + 2k/3 + l/2)]$$
$$\times [Zn^2 + O^2 + 2 \; ZnO \; \cos2\pi\mu l], \quad (4)$$

in which Zn and O represent scattering amplitudes of the corresponding nuclei. When the previously determined values[8] of the scattering amplitudes, +0.58 for Zn and +0.61 for O, are substituted in (4) the expression reduces to:

$$F = 17.8 + 10^{-24}[1 + \cos2\pi(h/3 + 2k/3 + l/2)]$$
$$\times [1 + \cos0.745\pi l]. \quad (5)$$

A cross-section curve calculated from the structure factors obtained by means of (5) and the multiplicity factors given in Table I gave a good fit with the experimentally determined curve. This confirmed both the magnitudes and the signs of the previously determined scattering amplitudes. Were the sign of Zn opposite from that of O, the last factor in (5) would be $(1 - \cos0.745\pi l)$.

In an x-ray diffraction pattern of ZnO, lines of relatively strong intensities are observed from planes such as (100), (002), (101), (102), (110), (103), (200), (112), (201), etc., whose Miller indices satisfy the following conditions—when l is odd, $h + 2K = 3n \pm 1$; when l is even, $h + 2K = 3n$, $3n \pm 1$ (i.e., any integer)—where $n = 0, 1, 2, 3 \cdots$.

Because of poor resolution of the rotating shutter device the peaks in the total neutron cross-section curve are actually caused by several planes which give strong reflections.

DISCUSSION OF RESULTS

As seen from the curves presented here, most of the diffraction effects are observed in the energy region 0.001 to 0.2 electron volt, which is covered by the rotating shutter device. While the resolution of the device is not comparable to that of the neutron or x-ray crystal spectrometer, enough diffraction peaks characteristic of the crystal system studied are observed that they

TABLE II. Scattering amplitudes of Ca, Ti, Tl, and Zn.

Element	Scattering amplitude	Remarks
	(units of 10^{-12} cm)	Based on scattering amplitude of:
Ca	+0.46±0.05	O, as +0.61×10⁻¹² cm
Ti	−0.25±0.03	C, as +0.67×10⁻¹² cm
Tl	+0.75±0.08	Br, as +0.56×10⁻¹² cm
Zn	+0.58	Same as reported previously (see reference 8)

permit unambiguous determinations of the magnitude and the sign of the scattering amplitudes as summarized in Table II.

The experimentally determined values of the total cross sections were somewhat higher than the corresponding calculated values for coherent scattering and absorption. The difference is significant and is a proper problem for future investigation.

This method of studying crystalline effects seems to be relatively feasible for those substances that have sufficiently low neutron absorption cross sections. An important application of this method can be made in the determination of the structures of compounds containing hydrogen and deuterium. By means of the usual x-ray diffraction methods the positions of all but the hydrogen and deuterium atoms can usually be determined. This limitation does not exist for neutrons, however, since hydrogen and deuterium have substantial scattering cross sections. If only a limited number of possible arrangements remain for the hydrogen and deuterium atoms after x-ray analysis, the method reported here might supply just the information required for a complete establishment of the structure.