

used for this. The problem is completely analogous to the absolute determination of the orientation of a non-centrosymmetric crystal, which has reflection symmetry. This problem has been solved for hexagonal CdS by Goodman & Lehmpfuhl (1968), who used a convergent-beam technique and a multiple-slice calculation for n -beam diffraction.

In the case of the interface analysis, it should be possible to predict for an interface inclined with respect to the beam which form is at the top of the crystal facing the electron gun. This can only be done when the difference in phase angle α is different from π . In the case of ordered lithium ferrite this is the case for reflections of type 012 or 203 when $\alpha = \pm\pi/2$. The problem is then reduced to a determination of the character of a stacking fault in f.c.c. metals (Hirsch, *et al.*, 1965). A systematic study of this problem for $\alpha = \pi/2$ has not yet been undertaken.

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Schwinger and Anomalous Scattering of Neutrons from CdS*

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Polarization-sensitive neutron scattering from CdS single crystals has been observed for several Bragg reflections. This effect arises from interference between neutron spin–neutron orbit (Schwinger) scattering and 90° phase-shifted scattering due to such sources as absorption and a noncentrosymmetric crystal structure. The observed flipping ratios are in excellent agreement with those calculated on the basis of the accepted conventions for the determination of absolute configuration by X-ray or neutron diffraction. Possible application of the Schwinger scattering to the routine determination of absolute configurations is discussed.

Introduction

Polarized neutron diffraction from vanadium crystals (Shull, 1963) has given evidence for a polarization-sensitive scattering amplitude that is both asymmetric and dephased by 90° with respect to ‘normal’ scattering. This effect (Schwinger scattering) has been attributed

to a neutron spin–neutron orbit interaction with the atomic Coulomb field.

We have performed a similar experiment with a crystal of CdS, a system for which the Schwinger scattering terms of cadmium and sulfur combine with the imaginary components of the scattering amplitude due to the cadmium resonance absorption and the noncentric sulfur positions. The polarization-sensitive scattering was indeed readily observed and its amplitude found in good agreement with that calculated.

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Anomalous scattering

It is well known that the scattering amplitude of a radiation (be it neutrons, or X-rays, or electrons) from an atom or a nucleus is wavelength-dependent, and in general complex.

In the theory of X-ray scattering (James, 1965), the incoming radiation is usually described by a plane wave

$$u(\mathbf{r}, t) = u \exp i(\omega t - \mathbf{K} \cdot \mathbf{r}) \quad (1a)$$

where ω is the frequency, \mathbf{K} the wave vector of the wave. Such a wave is scattered by an appropriate center with amplitude

$$b = b_r + ib_i \quad (2a)$$

where $b_r > 0$ above the resonances and

$$b_i = \frac{|\mathbf{K}|}{4\pi} \sigma_T \quad (3)$$

where σ_T is the total cross section; thus b_i is positive. In this first setting, the scattering vector is defined by

$$\mathbf{k} = \mathbf{K}' - \mathbf{K} \quad (4a)$$

where \mathbf{K} is the wave vector of the incident, \mathbf{K}' , the wave vector of the scattered wave.

In nuclear physics (Blatt & Weisskopf, 1952) and neutron scattering theory (Marshall & Lovesey, 1971), the incoming plane wave is usually defined by

$$u(\mathbf{r}, t) = u \exp i(\mathbf{K} \cdot \mathbf{r} - \omega t) \quad (1b)$$

The scattering amplitude then becomes

$$b = b_r - ib_i \quad (2b)$$

with b_r , b_i defined as in the first setting, but the scattering vector is defined by

$$\mathbf{k} = \mathbf{K} - \mathbf{K}' \quad (4b)$$

The observable quantities as obtained in the two settings are the same. For example, the cross section for coherent scattering from a crystal is proportional to

$$|F|^2 = \left| \sum_n b_n \exp i\mathbf{k} \cdot \mathbf{r}_n \right|^2 \quad (5)$$

where b_n are the scattering amplitudes of the atoms in the crystal cell at positions \mathbf{r}_n . If we set $b_n = b_{nr} - ib_{ni}$ (second setting)

$$|F|^2 = \left| \sum_n (b_{nr} \cos \varphi_n + b_{ni} \sin \varphi_n) \right|^2 + \left| \sum_n (b_{nr} \sin \varphi_n - b_{ni} \cos \varphi_n) \right|^2, \quad (5a)$$

where $\varphi_n = \mathbf{k} \cdot \mathbf{r}_n$. The same result is obtained, by reversing the sign of b_i and the direction of \mathbf{k} , for the first setting. For centrosymmetric crystals an inconsistent reversal of the sign of k or b_i is not important; it is, however, for polar or noncentrosymmetric crystals, for which the anomalous scattering allows the absolute determination of the positions \mathbf{r}_n . This point can be clarified by considering X-ray scattering from

ZnS (Coster, Knol & Prins, 1930), or – as will be done in the present article – the neutron scattering from CdS (Peterson & Smith, 1961).

CdS has a wurtzite structure, with Cd in the positions $000, \frac{1}{3}, \frac{2}{3}$ of its hexagonal cell, while sulfur has approximately the positions $00\frac{1}{3}, \frac{1}{3}, \frac{2}{3}$. One of the isotopes of Cd (^{113}Cd) exhibits a very large cross section for neutrons in the thermal region. The structure factor for the $00l$ reflections is, in the second setting

$$F_{00l} = b_{r\text{Cd}} - ib_{i\text{Cd}} + b_s \exp(-i3\pi l/4) \quad (6)$$

if the polar c axis is chosen in real space parallel to $\mathbf{K}' - \mathbf{K}$. Thus, by measuring the intensities of the $00l$ and the $00\bar{l}$ lines, the direction of the polar axis can be determined. For example, for the 00 ± 2 pair,

$$\begin{aligned} |F_{002}|^2 &= |b_{r\text{Cd}}|^2 + |b_{i\text{Cd}} - b_s|^2 \\ |F_{00\bar{2}}|^2 &= |b_{r\text{Cd}}|^2 + |b_{i\text{Cd}} + b_s|^2. \end{aligned} \quad (7)$$

Numerical values of the calculated intensities are reported in Table 1. If the assignment of the signs of b_i and \mathbf{k} is done incorrectly – if for example b is defined in the second setting, \mathbf{k} in the first setting – the same intensities are calculated only if the polarity of the c axis is reversed.

Table 1. *Calculated and observed neutron flipping ratios for the 00l Bragg reflections of CdS*

hkl	Hand	$ F_N _{\text{calc}}^2$	R_{calc}	R_{meas}
002	Right	0.170	0.995	0.993 ± 0.003
00 $\bar{2}$	Left	0.170	1.005	1.008 ± 0.004
00 $\bar{2}$	Right	0.318	0.983	0.986 ± 0.003
00 $\bar{2}$	Left	0.318	1.017	1.015 ± 0.004
004	Right	0.025	0.933	0.925 ± 0.009
00 $\bar{4}$	Right	0.025	0.933	0.941 ± 0.008
006	Right	0.318	0.985	0.984 ± 0.005
00 $\bar{6}$	Right	0.170	0.997	1.000 ± 0.004

The necessity for taking great care that a sign reversal does not occur when working out absolute coordinates is well known. However, even fairly recently a serious question has been raised (Tanaka, Ozeki-Minikata & Nakagawa, 1972) concerning the correctness of absolute configuration determined by the X-ray method. The present discussion is intended to demonstrate the essential equivalence and yet independence of the neutron method for absolute determinations. The few neutron determinations that have been made are in full accord with X-ray findings.

Schwinger scattering

Schwinger scattering was first reported for a vanadium crystal (Shull, 1963) where the effect, though quite small, was clearly established. In addition a brief report of Schwinger scattering for the 004 reflection of CdS and several reflections of quartz where the effects are much larger has been given (Shull, 1967). Our interest in further examination of the Schwinger effect is largely

in terms of its possible application to the determination of absolute configuration.

The theory of the electrostatic scattering of neutrons was originally given by Schwinger (1948) and later expanded and refined for scattering of thermal neutrons by solids (Blume, 1964; Obermair, 1966, 1967; Lovesey, 1969). The scattering amplitude for nuclear and electrostatic coherent scattering is (Lovesey, 1969).

$$F = F_N(\mathbf{k}) + i \frac{\gamma e^2}{2mc^2} \mathbf{P} \cdot \hat{\mathbf{n}} |\cot \theta| F_E(\mathbf{k}) + F_{\text{Foldy}} \quad (8)$$

when F_N is given by expression (5), and

$$F_E(\mathbf{k}) = \sum_n [Z_n - f_n(\mathbf{k})] \exp i\mathbf{k} \cdot \mathbf{r}_n. \quad (9)$$

Z_n is the charge of the nucleus at position \mathbf{r}_n , and $f_n(\mathbf{k})$ the form factor of its atomic electrons, as in X-ray scattering. The second term (Schwinger scattering) is imaginary, and antisymmetric, since it does not correspond to an absorption. The antisymmetric character of the scattering amplitude is given by the unit vector $\hat{\mathbf{n}}$, which is defined by

$$-\mathbf{k} \times \mathbf{K} = \hat{\mathbf{n}} K^2 |\sin 2\theta| \quad (10)$$

where θ is the Bragg angle. As has been noted (Shull, 1963), $\hat{\mathbf{n}}$ has opposite directions when the scattering vector \mathbf{k} is at the left or the right of the incident vector \mathbf{K} , and thus the Schwinger scattering provides a unique external probe for the determination of the phases inside the crystal. The amplitude of the Schwinger scattering is quite small, since its coefficient, $\gamma e^2/2mc^2 = -1.46 \times 10^{-4}$ in units of 10^{-12} cm ($\gamma = -1.91$, gyromagnetic ratio of the neutron). However, since the effect depends on the polarization \mathbf{P} of the incoming neutron, it can be detected by comparing the cross sections for neutrons polarized in one direction, and then in the opposite one. The third term in expression (8), F_{Foldy} , is of the same order of magnitude as the second, but is real and polarization independent. Hence there is no sensitive way to detect it; from the practical point of view, it can be neglected. The above formulas are valid in both settings; the choice of a setting implies the definition of \mathbf{k} in equation (10).

It is now easy to show in which sense the Schwinger scattering can help in the determination of the polar axis in CdS. Let us choose the second setting and suppose that the intensities of the $00l$ reflections are measured at the right, so that $\hat{\mathbf{n}}$ points down with respect to the scattering plane. The ratio of the intensities for neutrons with polarization up and down (flipping ratio) is

$$R_{00l} \simeq 1 + 2 \operatorname{Im} [F_N(00l) S_E^*(00l)]^2 / |F_N(00l)|^2 \quad (11)$$

with

$$S_E(00l) = p_{\text{Cd}} + p_{\text{S}} \exp(-i3\pi l/4) \quad (12)$$

and

$$p_n = \frac{-\gamma e^2}{mc^2} |\cot \theta| [Z_n - f_n(00l)]. \quad (13)$$

Note that p_n is positive. In particular, for the 00 ± 2 pair

$$\begin{aligned} (R_{002})_{\text{right}} &= 1 - 2[p_{\text{S}} b_{r\text{Cd}} + p_{\text{Cd}}(b_{i\text{Cd}} - b_{\text{S}})] / |F_N(002)|^2 \\ (R_{002})_{\text{right}} &= 1 - 2[-p_{\text{S}} b_{r\text{Cd}} + p_{\text{Cd}}(b_{i\text{Cd}} + b_{\text{S}})] / |F_N(00\bar{2})|^2 \end{aligned} \quad (14)$$

Thus the flipping ratios for the reflection pair are different and can be used to determine the polar-axis direction if the sensitivity is adequate. It is clear that simple intensity comparisons of appropriate $00 \pm l$ pairs would serve the same purpose; however, the flipping-ratio experiment, because of its higher intrinsic accuracy, is to be preferred.

The experiment

The flipping ratios R of the $00l$ reflections from a single crystal of CdS were measured at room temperature in the Solid State Polarized Neutron unit at the CP-5 reactor of Argonne National Laboratory. The layout of the instrument is illustrated in Fig. 1. The polarizer – a magnetized Co-Fe crystal – is kept in a magnetic field pointing down. In such condition, the polarization of the monochromatized neutrons (opposite to the direction of their magnetic moments) is up (Marshall & Lovesey, 1971). The polarization of the neutrons can be reversed by energizing the flipper. The sample was a thin single-crystal plate of CdS, of dimensions approximately $10 \times 8 \times 1$ mm and the c crystal axis was normal to the plate. The crystal was mounted on a goniometer head, oriented to bring the c axis horizontal, and diffracted intensities from the 00 ± 2 pair were checked to identify the polar-axis direction. The sample crystal was kept in a weak magnetic field (~ 25 Oe) in order to keep the neutrons polarized along their path. In view of the very weak magnetic susceptibility of CdS, such a field does not give rise to a detectable magnetic alignment in the crystal. In all measurements, the ratio was taken of the diffracted intensities for neutrons with polarization up *versus* those for neutrons with polarization down. Most of the measurements were taken with the wave vector \mathbf{K}' at the right of \mathbf{K} ; the flipping ratio for the 00 ± 2 reflections was also measured at the left, in order to recheck the symmetry of the Schwinger scattering ($R_{\text{left}} = 1/R_{\text{right}}$).

The calculated flipping ratios assume the polar axis direction determined from the intensities of the diffracted peaks. For the wavelength used ($\lambda = 1.036$ Å) the values used for the nuclear amplitudes were (Peterson & Smith, 1961): $b_{r\text{Cd}} = 0.375$; $b_{i\text{Cd}} = 0.13$; $b_{\text{S}} = 0.285$, in units of 10^{-12} cm. The X-ray form factors, appearing in expressions (9) and (13), were taken from *International Tables for X-ray Crystallography* (1962).

The calculated and measured values of the flipping ratio R , are presented in Table 1. The excellent quantitative agreement over all the observations is convincing evidence that the Schwinger scattering and its right-left asymmetry is being observed. The signal (defined as

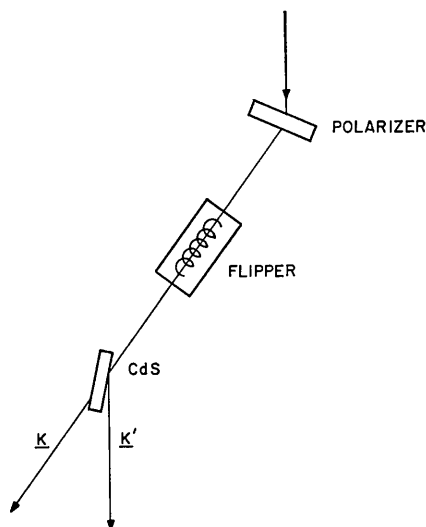


Fig. 1. Schematic diagram of the polarized-beam instrument indicating relative directions of vectors K and K' . View is from the top.

$R-1$) is one or two orders of magnitude larger than that observed in the first measurements (Shull, 1963); hence the observations were readily made. In addition, it is clear that the observed flipping ratios for polar pairs such as 00 ± 2 and 00 ± 6 discriminate between and identify the pair members, and hence can be used for polar axis or more generally absolute configuration determination. The statistical error of the signal indicated in Table 1 is quite large. Such error is quite close to the mean-square error from a set of repeated measurements and should be essentially the true error, since the polarized-neutron method utilizes the ratio of two cross sections, in the same experimental conditions. Higher precision would then only require longer counting time. Since three weeks of operation were needed to collect the presented flipping ratios for this quite absorbent crystal, an inconveniently long time would be required to improve the precision significantly. For these reasons, the data are just presented and compared with the values calculated for a fixed set of parameters.

Discussion

The experiment described here has shown that Schwinger scattering can be detected with ease if the proper conditions obtain. Although the Schwinger amplitudes, p_{Cd} and p_s , are of the order of only 1% of the nuclear amplitudes the intensity differences introduced by these terms are substantial because of the cross terms in equations (11) and (14). If the aim is

merely to detect Schwinger scattering one need only work with a structure which provides 90° phase shifts; the presence of a strong absorber is unnecessary. In addition the ratios p_n/b_{rn} must be substantially different for the atoms involved.

Schwinger scattering greatly expands the possibilities for application of neutron diffraction to absolute-configuration determination, since all atoms possess such imaginary scattering components and no strongly absorbing nuclei are required. However, a monochromatic beam of polarized neutrons is required, and that presently is obtained much less efficiently than an unpolarized beam. For this reason, polarized neutrons are unlikely to be commonly used for collecting a full set of intensity data on non-magnetic crystals (in such a case the absolute configuration is inherent in fully refined data). It is reasonable however to make flipping-ratio measurements on a few well-chosen reflections at the conclusion of a neutron structure determination, to provide the absolute configuration. As a rule of thumb, this procedure is advantageous, in comparison with the unpolarized-neutron method based on absorption, when $b_i < b_{Schwinger}$.

The excellent agreement obtained between theory and measurement for the case where an additional scattering term, the Schwinger effect, becomes significant provides additional reassurance, if needed, that the determination of absolute phase is being carried out consistently and correctly.

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