Study of Adsorption on Powders by Surface Differential Diffraction Measurements. Argon on $\text{Co}_3\text{O}_4$

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(Received 21 July 1981; accepted 22 December 1981)

Abstract

The amplitude and phase of a wave scattered by an adsorbed layer can be deduced from the modifications of the Bragg peak of the powder by adsorption. The treatment of experimental data involves the interpretation of a function of the extra intensity detected and has the advantages of an integrated intensity method. Powders containing crystallites limited by several types of faces can be studied. The $\text{Co}_3\text{O}_4$ sample studied is limited only by (110) and (111) faces of respective areas 11 and 27 m$^2$ g$^{-1}$. The (111) planes terminating crystallites contain oxygen covering a layer of cobalt in octahedral sites. Other possible terminating layers are ruled out for (111) planes. The structures of the bidimensional layers of argon on (110) and (111) planes are determined.

Introduction

The technique discussed in this paper consists of the determination of the difference between the diffraction patterns of a powdered solid with and without adsorbed species (Kjems, Passell, Taub & Dash, 1974). The surface differential pattern presents two types of features: surface peaks which are broad and unsymmetrical, and peaks located at the same angle as the peaks of the substrate, which we shall call Bragg-peak modifications (BPM). Surface peaks provide the same information as bulk peaks and the structure of the adsorbed lattice can be deduced from them. From the shape of the BPM one can deduce the phase of the waves scattered by the adsorbed layer with respect to the waves scattered by the substrate. If all the adsorbed scatterers are in the same plane the shape of the BPM gives the location of the adsorbed layer with respect to the substrate (Thorel, Croset, Marti & Coulomb, 1976). If the adsorbed layer is more complex, BPM and surface peaks have to be used jointly to obtain information on its structure.

Surface differential diffraction was first applied to the study of physisorption on graphite. Most of the faces limiting graphite have the same orientation perpendicular to the c axis. One therefore deals with a single type of face. We have shown, however (Beaufils & Barbaux, 1981), that more complex cases could be treated. To that purpose we used one special property of the BPM: when the adsorbed lattice is not in registry with the substrate surface lattice, only Bragg reflections on reticular planes of the substrate parallel to the adsorbing planes are modified. In that case the conclusion is unambiguous: If the BPM exists, the corresponding face also exists. We also showed that, in that out-of-registry case, it was possible to deduce the area of the corresponding face from the integrated intensity of BPM. This method works only if one is sure that all adsorption is out of registry. When the sum of the areas of all the faces is equal to the area deduced from an adsorption isotherm, this can be taken as a confirmation of the validity of the hypothesis. Another limitation comes from the fact that for certain shapes the integrated intensity of the BPM is zero.

The aim of the present paper is to show that these limitations can be released. First a theory is developed to calculate the contribution of an adsorbed layer to the modification of a Bragg reflection on a plane which is not parallel to the adsorbing plane. A method of accurate treatment of the shape of the BPM is also given. In this in-registry case there is no more one-to-one correspondence between BPM and adsorbing faces. Direct calculation of the properties of each face is not possible and one has to build a model and check that it can be fitted to experimental data.

The possibility of this model building is demonstrated with the example of the adsorption of argon on $\text{Co}_3\text{O}_4$. The choice of $\text{Co}_3\text{O}_4$ may appear surprising because it is rather complex: $\text{Co}_3\text{O}_4$ has $\text{Co}^{2+}$ and $\text{Co}^{3+}$ in a spinel lattice. The main reason for this choice is that other experiments suggested that its surface has very reproducible properties: The rate of catalytic oxidation of methane, per m$^2$ of catalyst, is...
Theory

The theory presented here is simply an adaptation to the surface case of principles given in crystallography textbooks.

Let \( A_c \) and \( A_r \) be the waves scattered by the crystal and the adsorbate on one of its faces respectively. The intensity of the difference pattern corresponding to this face is proportional to

\[
|A_c + A_r|^2 - |A_c|^2 = (A_c A_r^* + \text{c.c.}) + |A_r|^2.
\]

The second term corresponds to surface peaks. We restrict ourselves to the study of

\[ AJ = A_c A_r^* + \text{c.c.} \]

The shape of the scattering object \( X \), surface or bulk crystal, is expressed through the function \( G_x(\mathbf{r}) \) equal to 1 if the extremity of \( \mathbf{r} \) is inside \( X \) and to 0 if it is outside. The amplitude can be written:

\[
A_x(s) = \sum_{j \in X} b_j \exp(2\pi i s \cdot \mathbf{r}_j) = \sum_{j \in X} b_j \exp(2\pi i s \cdot \mathbf{r}_j) G_x(\mathbf{r}_j),
\]

where \( s \) is the scattering vector and \( \sum_{j \in X} \sum_{\beta \in X} \) are summations extended to the object \( X \) or to all space respectively.

For a planar surface carrying an adsorbate, the object is the surface provided with a sufficient thickness \( E \) to contain the adsorbate. A physical meaning can be given to \( \sum_{j \in X} \) by considering that from the bidimensional lattice of the adsorbate is generated a 3D lattice by translations of length \( -2E, -E, E, 2E, \ldots \) of the 2D lattice in a direction perpendicular to the plane.

Rewriting \( A_x(s) \) as

\[
A_x(s) = \int \sum_{j \in X} b_j \exp(2\pi i s \cdot \mathbf{r}) G_x(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}_j) d^3r,
\]

where \( \delta(\mathbf{r} - \mathbf{r}_j) \) is the 3D delta function, one obtains

\[
A_x(s) = \sum_{h,k,l} F_X(s_{hkl}) G_x(s - s_{hkl}) \exp[2\pi i(s - s_{hkl}) \cdot \mathbf{D}_X].
\]

where \( s_{hkl} = (h; k; l) \) = vector of the reciprocal lattice of \( X \), \( F_X(s_{hkl}) \) = structure factor of \( X \), \( V_X \) = volume of the unit cell of \( X \), \( G_x(s) \) = Fourier transform of \( G_x(\mathbf{r}) \), and \( \mathbf{D}_X = \mathbf{D}_c = 0 \), or \( \mathbf{D}_X = \mathbf{D}_F \), the vector from the centre of the crystallite to the centre of the face (both are supposed centrosymmetric).

This formula is obtained provided that the centre of the object is chosen as origin for the definition of \( F_X \) and \( G_x \), the centre \( O' \) of the face must coincide with the origin of the crystal unit cell containing \( O' \). Otherwise other phase factors appear when associating \( A_c \) and \( A_r \) (See Fig. 1.)

To obtain the total intensity, one has to sum the contribution of all the faces of a crystallite and to sum the contribution of all the crystallites. The second summation -- powder averaging -- is equivalent to an integration over all directions of \( s \) for a given value of \( |s| = 2 \sin \theta; \theta \) (2\( \theta \) = scattering angle) and multiplication by the factor \( N_c / 4\pi N_c \), \( N_c \) is the number of crystallites, if we assume that all grains are spherical and have the same diameter.

\[ G_c(s - s_c) \text{ is non zero only when } s \text{ is close to } s_c. \]

where \( h \) and \( r \) are indices of vectors perpendicular and parallel to \( s_c \). The element of solid angle containing \( s \) is

\[
d\Omega_s = \frac{d^2 \delta s_h}{|s|^2} = \frac{\lambda^2}{4 \sin^2 \theta_0} d^2 \delta s_h.
\]

The integration over all directions of \( s \) will be a sum of integrations in the neighbourhood of all the \( s_c \) of the same length, that is all the \( s_c \) of the same form \( \{h k l\} \). Finally, the intensity scattered at the angle \( 2\theta \) will be proportional to

\[
\int \sum_{\text{for all } \{hkl\}} (\Delta I + \Delta I^*) d\Omega = \sum_{\text{for all } \{hkl\}} \Delta I + \Delta I^*,
\]

\[
\Delta I = \frac{N_c \lambda^2}{4\pi \sin^2 \theta_0} \frac{F_c}{V_c} \frac{F_r^*}{V_r} \times \int G_c(\delta s) G_r(\delta s) \exp(-2\pi i \delta s \cdot \mathbf{D}) d^2 \delta s_h.
\]

We shall omit the explicit calculation of this integral for model shapes of crystallites and the discussion of the result because this would not bring any new result. Our method of treatment of data consists precisely of avoiding consideration in detail of the shape of the line by using appropriate integrals. These integrals have properties comparable to those of integrated intensities.

Usually one calculates the integrated intensity

\[ \int \Delta I(\theta) d\theta. \]

We know that

\[ d|\delta s| = d\delta s_h = (2 \cos \theta_0; \lambda) d\theta. \]

The integrated intensity will thus be an integration of \( d\Omega \) in all space, the volume element being

\[ d^2 \delta s_h d\theta = (\lambda; 2 \cos \theta_0) d^2 \delta s_h d\delta s_h = (\lambda; 2 \cos \theta_0) d^3 \delta s_h. \]
However, the integrated intensity may be 0 in certain cases and does not contain enough information on the phase of the $\Delta I$ terms.

To obtain more complete information, we calculate

$$Q = \int \Delta I(\theta) \exp[i\omega(\theta - \theta_0)]d\theta,$$

where $\theta_0$ is the centre of the Bragg peak of the substrate and

$$\omega = 2\pi D' \cos \theta_0/\lambda.$$

$\omega$ is related to the width of the line.

$$Q = \frac{N_C}{4\pi} \frac{\lambda^3}{\sin^2 \theta_0} \cos \theta_0 \frac{F_C F^*_F}{V_C V_F} K,$$

$$K = \int G_x(\delta s)G_y(\delta s) \exp[-2\pi i(\delta s \cdot D + D' \delta s_c)]d^3\delta s.$$

Let $D'$ be a vector of length $D'$ and direction $s_c$.

$$D' \delta s_c = D' \delta s.$$

$\psi$ is the angle between $D$ and $D'$.

$$K = \int \int \exp[2\pi i(r + r' - D + D')] \delta s$$

$$\times G_x(r)G_y(r')d^3\delta s d^3r d^3r'$$

$$= \int \int \delta (r + r' - D + D')G_x(r)G_y(r')d^3r d^3r'$$

$$= \int G_A(-r + D - D')G_B(r)d^3r.$$

The calculation of $K$ is illustrated in Fig. 1: $K$ is the volume common to the crystallite and to a surface of thickness $E$, area $S$, displaced by the translation $D-D'$ from the centre of the grain.

We write

$$K = ESF_{G_x}.$$

$F_{G_x}$ varies from 1 for $\psi$ small to 0 for $\psi$ greater than $\pi/2$.

When $\Delta I$ is replaced by $\Delta I^*$, $F_{G_x}$ is zero in the interval $(\pi/2, \pi)$ instead of $(0, \pi/2)$. Thus $Q'$ obtained by replacing $\Delta I$ by $\Delta I^*$ in the expression of $Q$ is not the conjugate of $Q$.

In practice the measured quantities depend on the neutron flux counted by the monitor, the efficiency of the detectors, their geometry, etc. Let $P$ be the integrated intensity of the Bragg peak of the substrate. It will depend on the same factors. The ratio $(Q + Q')/P$ will not depend on these factors. $R = (Q + Q')/P$ is a complex number. The real and imaginary parts of it are determined separately from the data. $R$ is a function of $D'$ calculated for each BPM. It is completely specified as $R(\text{type of } hkl)$ ($D'$).

The final expression for $R$ is

$$R = \frac{V_C}{M} \sum_{\text{faces}} F_{S_F S_C} \sum_{\text{types of } hkl} F_{S_F S_C},$$

where $S_{TF} = \text{total area of a face of one type, that is parallel to reticular planes of a given form } \{h'k'l'\}$, $V_{FC} = \text{total volume of the crystallites, } S_{TC}/\rho V_{FC} = \text{the specific area of the type of face, } \rho = \text{crystallographic density, } M = \text{multiplicity of the form } \{hkl\}$.

Two methods of treatment of the $R$'s can be envisaged:

1. We notice that, apart from certain numerical factors, the product $RF_{G_x}$ is essentially a surface structure factor $F_{S_F}$. By a Fourier transform one could go from $F_{S_F}$ to the positions and scattering lengths of the scatterers, multiplied by certain coefficients. However, the interest of this method is very limited, even if the data are reasonably good, because certain $hkl$ reflexions are forbidden in the substrate pattern. Thus certain BPM cannot be observed because there is no Bragg peak and certain Fourier components would be missing.

2. Given a model of the surface depending on the specific area of the various faces and on the positions of the adsorbed scatterers, one can calculate the $R$'s and adjust the parameters of the model to fit calculated $R$'s to the experimental ones. This method will be illustrated in the case of the adsorption of argon on Co$_3$O$_4$.

Experimental

Co$_3$O$_4$ was prepared by thermal decomposition of cobalt carbonate in air. Before the experiment it was heated for 4 h at 670 K in oxygen and cooled under oxygen. An adsorption isotherm of argon at 80 K was then made. From BET theory (Brunauer, Emmett & Teller, 1938) it was concluded that the argon monolayer at this temperature contained $2.1 \times 10^{20}$ argon atoms g$^{-1}$, 10 g of sample were placed in an aluminium container, with walls of thickness 0.1 mm, having a diameter of 20 mm. The container was connected to a gas handling manifold and attached to a dysplex refrigerator. To avoid reduction of the sample, air was evacuated at room temperature by a very brief pumping. The introductions of $^{36}$Ar (chosen for its large scattering length) were made at 80 K. The amount of $^{36}$Ar introduced was determined with the help of a calibrated volume and a baratron pressure gauge. Four diffraction patterns were recorded, all at 20 K: Co$_3$O$_4$ without argon, Co$_3$O$_4$ with 1.9, 2.1 and $2.3 \times 10^{20}$ argon atoms g$^{-1}$. 

Fig. 1. Calculation of $F_{G_x}$. The dashed area represents the common volume described in the text. $A, B, C$: volumes inside which $G_x(r)$, $G_A(-r + D), G_A(-r + D - D')$, respectively, not equal to 0.
Neutron diffraction patterns were recorded at ILL, using the D1B powder diffractometer. The fixed multidetector of this instrument is well suited to this type of experiment. The experimental procedure of recording diagrams and the calculation of difference patterns have been described in our preceding paper (Beaufils & Barbaux, 1981).

Neutrons are strongly absorbed by Co₃O₄. A correction for the decrease of incident flux due to absorbed and scattered neutrons was therefore required. The formula of Rouse, Cooper, York & Chakera (1970) was used for this purpose. The extinction of Co₃O₄ was calculated from the amount present in the container and the known total cross sections. Because of our method of treatment of data involving the calculation of a ratio of integrated intensities, the correction of Co₃O₄ absorption was not directly needed. However, the addition of argon noticeably changed the extinction of the sample. The correction for argon was calculated by differentiating the formula of Rouse et al. and depended on the extinction of Co₃O₄.

In Fig. 2 is represented the difference pattern of Co₃O₄ covered with 2.1 x 10²⁰ argon atoms. The difference patterns for the two other coverages are very similar. All the Bragg peaks of the Co₃O₄ are modified by adsorption. A surface peak S1 with a maximum at θ = 11.6° appears clearly. The corresponding second-order surface peak S2 can also be recognized with a maximum around θ = 21°, but it is too flat to be quantitatively treated.

The peak at θ = 9.2° is indeed a surface peak rather than a BPM for the following reasons. The 200 reflexion is forbidden in the spinel structure. It appears because neutrons have a magnetic moment which interacts with Co²⁺ magnetic moments and because, below 40 K, these moments show antiferromagnetic order (Roth, 1964). Argon, having no magnetic moment, cannot modify the purely magnetic 200 peak in an experiment dealing with unpolarized neutrons. The possibility that argon physisorption modifies the distribution of electrons amongst cobalt ions at the surface has to be ruled out. No possible impurity of argon could produce this effect because it would have to show reducing properties to produce more Co²⁺.

Lastly, the 200 BPM could be an artefact if the effect of attenuation of the neutron beam by adsorbed argon were underestimated. However, this would require an error on the attenuation which is very unlikely. One possibility is left: This peak is a surface peak S3: its asymmetry is not very apparent because S3 overlaps S1.

**Determination of the experimental R’s**

Before calculating integrated intensities for the substrate pattern and Fourier transforms of the different pattern lines, a background was subtracted. The background was assumed linear except for the 220 peak which lies on the tail of the surface peak S1. The calculation of this tail is given when we discuss surface peaks to determine the positions of adsorbate atoms. The linear background was estimated from the value of the signal in parts of the pattern considered as flat in the neighbourhood of the peak.

The errors affecting the R’s are the following:

- **Statistical error on the signal.** An upper bound of this error for ∫ |I| cos(θ − θ₀) dθ is obtained by taking the statistical error on ∫ I dθ and multiplying it by √2.

- **Statistical error on the background.**
  - Assumption that a flat part of the pattern gives the background. This neglects the wings of the line.
  - Aluminium lines: the parameter of the aluminium lattice being close to one half that of the Co₃O₄ lattice, some of the lines of the Co₃O₄ patterns are contaminated by Al lines. When the difference between patterns is made, these contributions do not cancel rigorously because the aluminium on the front and on the back of the sample with respect to the neutron beam is not affected in the same way by the attenuation due to the adsorbate. Consequently R for 222 and 400 could not be computed. For 440, some errors due to the aluminium are probably left but cannot be estimated.

- **θ₀ evaluation: error negligible.**

- **Overlap of neighbouring lines:** 533 overlaps 622 for which R could not be used.

The errors in R amplitudes are, except for Al contamination, and neglect of wings, of the order of 0.03. The errors on phases are not affected by Al contamination. They are of the order of 0.08 rad for 111 and 0.25 for other lines.

The value of R for 111 had to be corrected for the magnetic contribution to the denominator, which is
deduced from the corresponding value for the purely magnetic 200 line. No other line has to be corrected for magnetism because this contribution decreases rapidly under the influence of the form factor.

Definition of the model

To calculate the $R$’s we need the following data:
- Size and shape of the grains to calculate $F_G$.
- Faces limiting the grain.
- Position of scatterers on each face with respect to the substrate.

For the calculation of $F_G$, it is assumed that the grain is spherical and that the face is plane, bounded by a circle. We have in addition taken account of the presence of grains of different sizes, by replacing $F_G$ in the expression of $R$ by an averaged $\langle F_G \rangle$.

The distribution of diameters used in calculating $\langle F_G \rangle$ was obtained as follows: The shape of some lines of the diffraction pattern of our sample was determined using the high-resolution powder diffractometer D1A at ILL. Data were corrected using the instrument program (Hewat, 1978). Taking the second derivative of the Fourier transform of the 400 line gave us a thickness distribution (Bertaut, 1950) from which we deduced a distribution of diameters assuming the spherical shape. The distribution was centred at a diameter of 55 Å with a width of 30 Å.

The choice of the limiting faces was based on the following considerations:
1. If the adsorbed lattice is not in registry with the surface lattice of the substrate, one has to consider that there exist limiting faces parallel to (100), (110), (111), (311) planes. The calculation of the number of scatterers on each of these faces from BPM is straightforward and the total number of scatterers according to this hypothesis is of the order of $6 \times 10^{20}$ argon atoms g$^{-1}$. This is three times the total amount introduced in the sample and this hypothesis must be ruled out.
2. If the adsorbed lattice is in registry with the surface lattice of the substrate, there is no need to consider a priori four types of faces. Monocrystals of Co$_3$O$_4$ large enough to have a recognizable shape have been prepared (Picard, Band, Besse & Chevalin, 1980). Only faces parallel to (110) and (111) planes were observed. It is not certain that our sample, being prepared in a very different way, has the same limiting faces, but we shall take that as a starting point for our model.

The model for the positions of scatterers was deduced from the consideration of surface peaks as explained below.

Positions of argon atoms

The reticular distances corresponding to surface peaks cannot be obtained directly by applying Bragg’s formula to the angle of the maximum. The theory of Warren (1941) shows that a small correction is needed. This correction depends on the size of the 2D crystallites. This size can be deduced from the width of the peak. The average size of the 2D crystallites is 6 nm. The reticular distances corresponding to the peaks $S_3$ and $S_1$ are 0.43 nm and 0.33 nm.

Fig. 3 and 4 show probable surface lattices in registry with the surface lattice of faces parallel to (110) and (111), respectively, showing the required reticular distances. Both faces contribute to the peak $S_1$. Only face (111) contributes to $S_3$. These lattices are used in our model.

Fitting procedure

The expression of $R(D')$ shows that the amplitude of the $R$’s is affected mainly by the area of the faces and depends little on the positions of the scatterers. The phase of the $R$’s behaves in the opposite way. Finally, the detailed dependence of $|R|$ on $D'$ reflects the shape and size distribution of the grains.

A detailed fitting of the $D'$ dependence would therefore give, in principle, a test of the shape and size
distribution model. The resolution of D1B and the low counting rates do not justify such an attempt. We have therefore considered only one $D'$ value for which the $R(D')$ were fitted. This value of $D'$ was chosen in the following way: For $D' = 0$ the phase of the $R$'s is always 0. When $D'$ increases the phases may vary and reach a plateau. Beyond the plateau, the phases are no longer significant because the amplitudes go to 0. The plateau region is the one where best use of the data is made to calculate the phase. $D'$ should be chosen in this region: $D' = 3.2$ nm.

The amplitudes and phases of the $R$'s were fitted together, using a least-squares method weighting each contribution according to its accuracy.

The parameters of the fit were the number of scatterers for each adsorbing face and the distance between the origin of the unit cell of the substrate close to the surface and the plane of adsorbate. The values of these four parameters are discussed below. Table 1 compares the experimental and calculated values of the $R$’s.

In addition, the effect of a translation of the adsorbate lattice in a plane parallel to the adsorbing face was considered. The $R$’s were calculated for one single face of fixed area moving in its plane. For certain reflections the phase and amplitude of $R$ remain constant. For other reflections the phase remains approximately constant only if a fixed point of the adsorbate lattice remains inside a certain domain. In passing from one domain to the other the phase can vary abruptly. The variation can amount to $\pi$. The variations of amplitude are smoother. Given the accuracy of the determination of $R$, it is not possible in general to locate precisely the adsorbate plane with respect to the substrate. To determine which domain is in agreement with the data, we compared four parameter fits for adsorbate lattices located in different domains. For the (110) face no clear-cut conclusion could be drawn. For (111) the situation is very clear as can be seen from the example given in Table 2.

### Terminating faces

We have assumed that the plane of the substrate lattice terminating a crystallite contained atoms of Co and O having the same positions as if they were in the bulk. We can provide no evidence for this hypothesis.

### Table 1. Best fit

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<td>111</td>
<td>0.68</td>
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<td>0.45</td>
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<tr>
<td>440</td>
<td>0.12</td>
<td>0.26</td>
</tr>
<tr>
<td>444</td>
<td>0.12</td>
<td>0.14</td>
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<tr>
<td>800</td>
<td>0.12</td>
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### Table 2. (111) adsorbate plane displaced by 0·14 nm in direction [110]

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If a redistribution of atoms or a change in the number of oxygens has taken place this has no visible effect on the patterns, provided that the surface remains stable during the adsorption of argon. We also assume that, on the surface, oxygen ions have the same radius as in the bulk. This would not be true with O$^-$ ions. Two types of planes can exist at the surface of the Co$_3$O$_4$ parallel to (110) planes. One contains Co$^{3+}$ and Co$^{2+}$ ions (Fig. 3), the second contains only Co$^{3+}$ ions. In both cases one can calculate the distance between argon and oxygen atoms. We assume that the argon atoms are in contact with four oxygen ions. The oxygen–argon distance is then 0.29 nm for the first plane and 0.38 nm for the second. The expected value ranging from 0.35 to 0.38 nm, the second plane is therefore the terminating plane.

For terminating (111) planes, six possibilities exist containing respectively per unit surface cell 12 Co$^{3+}$, 16 O$^{2-}$, 4 Co$^{2+}$, 4 Co$^{3+}$, 16 O$^{2-}$ in that order. The argon layer is on an oxygen plane covering a 12 Co$^{3+}$ plane, the relative positions of argon and oxygen is as shown in Fig. 4. In that case two types of argon exist: 2 of the argons sit in contact with three oxygen ions and 1 sit on top of an oxygen. For the first category the oxygen–argon distance is 0.35 nm. For the second it is 0.32 nm. In view of the presence of two types of argon atoms, we tried a five-parameter fit in which the distances of the two types of argon were allowed to vary separately, without obtaining a conclusive improvement; the two distances seemed to converge to close values.

### Areas

The other important parameter in fitting the $R$’s is the number of scatterers per face. We must first discuss the total number of scatterers which should be equal to the number of argon atoms introduced on the sample. The values calculated from BPM are 1.4, 1.9, 1.8 to be compared respectively to 1.9, 2.1, 2.3 ($\times 10^{20}$ atoms g$^{-1}$). The agreement at a coverage of 1 is satisfactory. When the coverage increases above 1 the apparent number of scatterers decreases. This is because a second layer begins to develop and the waves scattered by it do not have the right phase to add to those of the first layer. When the coverage is lower...
than 1 there is room for more disorder and the apparent number of scatterers calculated with this model decreases more rapidly than expected.

The number of scatterers can also be deduced from the area of a surface peak (Warren, 1941). To measure this area, the background has to be known precisely. The Warren theory predicts that the tail of the peak obeys a law $1 - \sin^2 \theta_0 / \sin^2 \theta = 12$. This law is well verified by experiment if a constant background is subtracted. Then the area of the peak is calculated. Only peak S1 can be treated in this way.

However, peak S1 is the superposition of two contributions; one for (110) has a multiplicity of four, the other for (111) has a multiplicity of two. The surface peak area gives only $S = 4 \times$ scatterer number (110) + $2 \times$ scatterer number (111). The value for a coverage of 1 is 4.8 to be compared with 6.8 deduced from BPM.

We conclude from this discussion that a monolayer is built, in the conditions of our experiment, for 2.1 $\times$ $10^2$ argon atoms g$^{-1}$. The area of the (110) face is 11 m$^2$ g$^{-1}$, that of the (111) face is 27 m$^2$ g$^{-1}$. The accuracy of these partial areas is probably very poor as can be seen from Table 1 (amplitudes).

**Conclusion**

The method of treatment of BPM presented in this paper has the advantage of integrated intensities: the statistical error is reduced and the correction for the resolution of the instrument is easier. The advantage is especially visible for phase determination and allows in our case the determination of distances of 0.35 nm with an accuracy of 0.01 nm. The alternative treatment of BPM is to fit peaks point by point (Rayment, Thomas, Bomchill & White, 1982). This second method can, if the accuracy of the data is sufficient, give more information, including a law of distribution of sizes of crystallites.

With our integral method it is possible to take into account all the contributions to a Bragg peak modification by adsorption and study complex solids exposing several types of faces. Thus the surface differential diffraction (SDD) method is no longer limited to layer compounds. It even appears that materials like Co$_3$O$_4$ which have grains of quasi-spherical shape have one advantage over graphite: the probable absence of orientation effects. The SDD method can be applied to any solid of sufficient area, if the structure of the bare solid is known in sufficient detail. It can be applied to solids placed in any environment, including the case of a porous electrode dipped in a liquid.

The information obtained includes the type of exposed faces, their areas, the nature of the limiting faces in the case of complex solids and structural data concerning the adsorbate. The interest in this information for the understanding of catalytic and electrochemical processes is obvious. In the case of a solid like Co$_3$O$_4$ and many other binary compounds, very few other methods are available because the surface of Co$_3$O$_4$ is reduced under vacuum.

The results obtained here call attention to the limitations of the present methods of evaluation of specific areas. It is possible to deduce from an adsorption isotherm the number of atoms or molecules per monolayer on one grain of solid. To deduce from that figure an area, one must know the average area occupied by one atom or molecule. For argon a value currently accepted is 0.152 nm$^2$, deduced from the argon radius in the solid phase. This is very different from the values of 0.216 and 0.189 nm$^2$ that we encountered in this paper.

We thank P. Convert and S. Heathman for their help in setting up the D1B and D1A experiments and B. Croset and C. Marti for stimulating discussions.

**References**


