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Direct Determination of Stacking Disorder in Layer Structures

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A stack of N identical, parallel, and equidistant layers is used as a simple model of a layer structure. Irregularities in the relative displacements $\boldsymbol{\delta}$ parallel to the plane of the layers correspond to stacking disorder. The stacking disorder is described by means of a set of functions $W_M(\boldsymbol{\delta})$ which measure the probability of finding a relative displacement $\boldsymbol{\delta}$ for layers M spacings apart. It is shown that x-ray diffraction data permit a direct determination of the Fourier coefficients of the functions W_M. Thus these functions can be synthesized and the nature of the stacking disorder directly deduced.

INTRODUCTION

IRREGULARITIES in the relative displacement of the layers parallel to their own planes occur in many crystals of layer structure type. This stacking disorder gives rise to characteristic features in the x-ray and electron diffraction patterns of such crystals. The purpose of this paper is to show that the specific nature of the stacking disorder can be directly deduced from the observed diffraction effects.

In order to demonstrate clearly the general principles upon which the method is based it is convenient to use a simple model of a layer structure. The extension of the method to layer structures of more general type can be made without serious difficulty.

A SIMPLE MODEL OF A LAYER STRUCTURE

Our model is a sequence of N identical, parallel, and equidistant layers. The periods within the layers will be denoted by $\mathbf{a}_1$ and $\mathbf{a}_2$, while $\mathbf{a}_3$ is the period in the third principal direction (not necessarily normal to the plane of the layers). The individual layers in the stack will be numbered consecutively by means of an index L_3, the layer $L_3=0$ being chosen arbitrarily. The symbol $\boldsymbol{\delta}_{L_3}$ will be used to represent the displacement, parallel to the plane of the layers, of layer L_3 relative to layer $L_3=0$.

The position vector of any atom in the crystal has the form

$$\mathbf{r}_j+L_1\mathbf{a}_1+L_2\mathbf{a}_2+L_3\mathbf{a}_3+\boldsymbol{\delta}_{L_3}.$$

$\mathbf{r}_j$ is the position vector of the jth atom within a unit parallelogram of a layer and L_1, L_2, L_3 are a set of three integers.

The model just described corresponds to an ordered layer structure if $\boldsymbol{\delta}_{L_3}$ varies periodically as the index L_3 is allowed to run through the sequence of integral value. We shall assume that the $\boldsymbol{\delta}$-values are not periodic, in which case the model corresponds to a layer structure with stacking disorder.

We shall assume that the distribution of $\boldsymbol{\delta}$-values throughout the stack is independent of the crystal surface. In order to study the consequences of this assumption we imagine the stack of layers to be periodically repeated in space. Our assumption implies that any sequence of N consecutive layers bodily removed from the periodic stack corresponds to a crystal specimen representative of the given disorder. Clearly there are N such different but statistically equivalent specimens. In discussing the disorder we shall therefore have to think in terms of the assembly of N specimens rather than in terms of a single specimen.

The stacking disorder for the assembly can be described by means of a series of probability functions $W_M(\boldsymbol{\delta})$, where $M=0, 1, 2, \cdots, N-1$. A function W_M represents the probability of finding a relative displacement $\boldsymbol{\delta}$ between two layers M spacings apart.

The displacement $\boldsymbol{\delta}$ can be expressed in the form $\boldsymbol{\delta}=y_1\mathbf{a}_1+y_2\mathbf{a}_2$ where $0\leq y_i<1$. Clearly $W_0=0$ for all values y_1, y_2 except $y_1=y_2=0$. Since the functions W_M are even and periodic functions we may set

$$W_M(y_1, y_2)=\sum_{H_1}\sum_{H_2} W^M{}_{H_1H_2}\cos 2\pi(H_1y_1+H_2y_2), \quad (1)$$

where the Fourier coefficients conversely are given by

$$W^M{}_{H_1H_2}=\int_0^1\int_0^1 W_M \cos 2\pi(H_1y_1+H_2y_2)dy_1dy_2.$$

THE X-RAY DIFFRACTION PATTERN

This section is devoted to a theoretical study of the x-ray diffraction patterns of structures with stacking disorder. Since each individual layer is assumed to be a fully ordered two-dimensional lattice we shall obviously find that the scattering is restricted to directions with "Miller indices" (H_1H_2z) when H_1 and H_2 (but not necessarily z) are integers. We shall show that the intensity of scattering in a direction (H_1H_2z) can be expressed in terms of the Fourier coefficients $W^M{}_{H_1H_2}$. Secondly we shall show that the individual Fourier coefficients can be deduced from the experimental data and that hence the probability functions W_M can be synthesized.

The mean intensity of the scattered x-rays from the assembly of N crystals discussed in the preceding section becomes

$$I(\mathbf{s})=NA(\mathbf{s})\textstyle\sum_M \cos\mathbf{s}\cdot M\mathbf{a}_3\langle\cos\mathbf{s}\cdot\boldsymbol{\delta}_M\rangle_{\text{Av}}. \quad (2)$$

In this expression $\mathbf{s}=2\pi(\mathbf{k}-\mathbf{k}_0)$ where $\mathbf{k}_0$ and $\mathbf{k}$ are the wave vectors of incidence and of scattering. $A(\mathbf{s})$ represents the intensity of scattering from a single layer.

It is convenient to set

$$\mathbf{s}=2\pi(H_1\mathbf{b}_1+H_2\mathbf{b}_2)+2\pi(p_1\mathbf{b}_1+p_2\mathbf{b}_2+z\mathbf{b}_3)$$

where H_1 and H_2 are integers and $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$ the vector set reciprocal to $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$. In this way the functions $I_{H_1H_2}(p_1p_2z)$ represent the intensity distribution in the reciprocal lattice.

The function $A_{H_1H_2}(p_1, p_2\, z)$ for given z has a maximum at $p_1=p_2=0$. The half width of this maximum depends upon the lateral dimensions of the layers. Unless the crystal dimensions parallel to the layers are of colloidal or subcolloidal order of magnitude one will not be able to observe the variation of $A_{H_1H_2}$ as function of p_1 and p_2. For this reason we shall deal not with the intensity $I_{H_1H_2}(p_1p_2z)$ but with the experimentally significant quantity $P_{H_1H_2}(z)$ defined by

$$P_{H_1H_2}(z)=\int\int I_{H_1H_2}(p_1, p_2, z)dp_1dp_2.$$

The expression for $P_{H_1H_2}$ becomes

$$P_{H_1H_2}(z)=I_0\delta VB_{H_1H_2}(z)\sum W^M{}_{H_1H_2}\cos 2\pi Mz. \quad (3)$$

The quantities $W^M{}_{H_1H_2}$ are the Fourier coefficients which were introduced in the preceding section. I_0 is the intensity of the incident beam and δV is the volume of a single crystal specimen, which for the sake of convenience is assumed to be so small that absorption and extinction can be neglected. The function $B_{H_1H_2}$ can be written in the form

$$B_{H_1H_2}=V^{-1}T|\psi_{H_1H_2}|^2$$

where $V=\mathbf{a}_1\cdot\mathbf{a}_2\times\mathbf{a}_3$, $\psi_{H_1H_2}$ the structure factor and $T=(1+\cos^2 2\theta)e^4/2m^2c^4R^2$ the Thomson scattering factor.

Experimentally one does not measure directly the power distribution $P_{H_1H_2}(z)$ in the reciprocal lattice, but rather the power $Q_{H_1H_2}(\alpha)$ in terms of a parameter α which is suitable for the particular experimental procedure which is used. The reduction of the observations $Q_{H_1H_2}(\alpha)$ to the reciprocal lattice distribution $P_{H_1H_2}(z)$ is, however, a trivial problem which involves the evaluation of the appropriate Lorentz factor.

Since $W^M{}_{00}=1$ for any M the function $P_{00}(z)$ will have maxima for integral values of $z=H_3$, and the half width of these maxima is determined by the total height of the stack of layers. In other words the stacking disorder has no effect on the reflections $(00H_3)$.

If the nature of the stacking disorder, i.e., each function W_M, is known, the calculation of the functions $P_{H_1H_2}(z)$ by means of Eq. (3) is a simple matter, and the nature of the stacking disorder can be found by a trial and error procedure. Equation (3) suggests, however, a direct method for the determination of the specific character of the disorder.

The distributions $P_{H_1H_2}(z)$ can be regarded as functions which are known from experiments, however, on a relative rather than absolute scale. The functions $B_{H_1H_2}(z)$ are known if the structure of each layer has been determined.

Hence, the quantities

$$D_{H_1H_2}(z)\equiv P_{H_1H_2}/I_0\delta VB_{H_1H_2}$$

are known functions except for a numerical scale factor. By the Fourier reciprocity theorem we have

$$W^M{}_{H_1H_2}=\int_{-\frac{1}{2}}^{\frac{1}{2}} D_{H_1H_2}(z)\cos 2\pi Mz dz.$$

Accordingly the probability functions W_M which characterize the stacking disorder can be synthesized. The unknown numerical scale factor can be determined from the requirement that W_M is everywhere positive and $\int\int W_M dy_1 dy_2=1$.

In most instances it is found that the functions W_M approach a limit W_∞ as M increases. It is therefore convenient to set

$$W_M=W_\infty+\Gamma_M$$

where accordingly Γ_M represents fluctuations at small values of M so that the Fourier coefficients $\Gamma^M{}_{H_1H_2}$ go towards zero with increasing M.

One sees readily that

$$\sum_M W^M{}_{H_1H_2}\cos 2\pi Mz=W^\infty{}_{H_1H_2}\sum_M \cos 2\pi Mz +\sum_M \Gamma^M{}_{H_1H_2}\cos 2\pi Mz.$$

Thus the functions W_∞ is generally to be associated with the sharp maxima, the functions Γ_M with the diffuse maxima of the functions $P_{H_1H_2}$.

If the function W_∞ is a constant, implying zero correlation between layers far apart, $W_{H_1H_2}=0$ unless $H_1=H_2=0$. Apart from the reflections $(00H_3)$ all maxima of $P_{H_1H_2}$ will then be diffuse.

The writer has used the method outlined above to determine the stacking disorder in several crystals of the layer structure type.

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Surface States and Rectification at a Metal Semi-Conductor Contact

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Localized states (Tamm levels), having energies distributed in the "forbidden" range between the filled band and the conduction band, may exist at the surface of a semi-conductor. A condition of no net charge on the surface atoms may correspond to a partial filling of these states. If the density of surface levels is sufficiently high, there will be an appreciable double layer at the free surface of a semi-conductor formed from a net charge from electrons in surface states and a space charge of opposite sign, similar to that at a rectifying junction, extending into the semi-conductor. This double layer tends to make the work function independent of the height of the Fermi level in the interior (which in turn depends on impurity content). If contact is made with a metal, the difference in work function between metal and semi-conductor is compensated by surface states charge, rather than by a space charge as is ordinarily assumed, so that the space charge layer is independent of the metal. Rectification characteristics are then independent of the metal. These ideas are used to explain results of Meyerhof and others on the relation between contact potential differences and rectification.

INTRODUCTION

THE generally accepted view[1] of the nature of the rectifying contact between a metal and a semi-conductor is illustrated in Fig. 1 which applies specifically to an excess semi-conductor. Figure 1a shows an energy level diagram of the metal and semi-conductor in equilibrium, but with the contact separated. The Fermi level is the same in both the metal and the semi-conductor. As shown, the work function of the metal, χ_1, is greater than the work function of the semi-conductor, $\chi_2{}^0$, so that there is a contact difference in potential, $\chi_1-\chi_2{}^0$. It is assumed that when the metal and semi-conductor are nearly joined, the potential distribution is as shown in Fig. 1b. A double layer is formed such as to give a potential drop, φ_0, from the metal to the interior of the semi-conductor equal to the contact potential difference.

This double layer is assumed to consist of a space charge region in the semi-conductor, extending to a depth of the order of 10^{-6} to 10^{-4} cm,

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[1] See, for example, N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940), Chap. V. The theory of rectification is due in large part to W. Schottky. The most important of his papers is Zeits. f. Physik **118**, 539 (1942).