Virtual Bragg Scattering: A Practical Solution to the Phase Problem in Diffraction

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It is found that appreciable multibeam effects are observable even when the Ewald sphere is quite far from any extra node in reciprocal space. It is proposed to use these effects for phase identification in mosaic crystals.

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It is a well recognized fact that in any scattering experiment the phase of the scattered radiation is lost, because in general the source is spatially incoherent and the detector is phase insensitive. Such is the case of Bragg diffraction from crystals, and constitutes the essence of what is normally called "the phase problem" in crystallography. In reality there are mathematical methods for extracting phases from a large number of reflections, but we still talk about a "phase problem" in the sense that we do not have a *physical* method capable of providing *direct* phase information, based on some principle in which the phase of a given reflection plays a basic recognizable role.

One situation in which the outcome of the experiment depends on the relative phases of two or more reflections is when several Bragg reflections are excited simultaneously. It has been recognized for a long time that in this situation, ordinarily referred to as N-beam diffraction, the phases are not lost and can be recovered, at least in principle.[1,2] It has been shown, for example, how phase effects can be unraveled from Pendellösung fringes deformed by three-beam diffraction.[3] There are, however, practical difficulties, and the progress has been, so far, rather limited.

A convenient geometry for studying N-beam effects is the symmetric Bragg case of diffraction (Fig. 1), in which a crystal, cut parallel to a set of (hkl) planes, is diffracting an incident monochromatic x-ray beam, and at the same time is slowly rotated around the scattering vector, so as to excite other reflections ($h'k'l'$) for which Bragg's law is also satisfied. If the "primary" reflection is weak, as is the case of the (222) forbidden reflection in silicon, or germanium, for example, strong variations are observed in the (222) intensity as a function of the azimuthal angle φ. The process which leads to these intensity fluctuations is called "Umweganregung" (detour radiation, abbreviated hereafter as umweg) and has been investigated in detail, from the kinematic point of view, by Cole, Chambers, and Dunn[4] in 1962. An effort to tackle the phase problem with use of the information contained in an umweg pattern was attempted by one of us (R.C.).[5] The general problem of N-beam diffraction in the Bragg case was solved in Ref. 5 and computational procedures were developed for calculating intensity profiles of umweg patterns, with excellent agreement between theory and experiment.

More recently a different method, again based on the general idea of N-beam diffraction, has been proposed,[6] in which a divergent-beam technique is used to generate diffracted lines on film. The crystal is set for diffraction in the Laue case, and phase information is extracted from anomalies due to N-beam effects.

Most crystals for which a real "phase problem" exists are far from being perfect, and it is not clear to what extent the methods described in Refs. 5 and 6 are applicable to mosaic crystals. Yet, multiple-beam effects are visible even in mosaic crystals, and within each mosaic grain the diffraction process is dynamic, and the phase information is preserved.

We want to propose in this paper a new method of attack to the phase problem based on the idea of "virtual Bragg diffraction."

The idea is basically the same as that described in Ref. 5, namely the umweg pattern is used as a

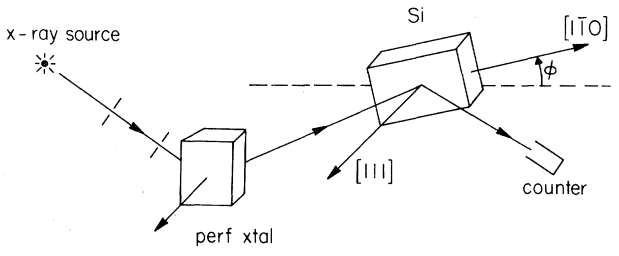

FIG. 1. Geometry of the experimental setup. The x-ray beam is monochromatized by a perfect flat crystal. The (222)-diffracted beam intensity varies as the crystal is rotated around the scattering vector, signaling the crossing of the Ewald sphere by reciprocal-lattice nodes.

source of phase information. Except that we do not consider the peak values of the umweg peaks, but confine our attention to the *tails* of the peaks observed in azimuthal scans. In other words, while the "primary" reflection [say, the (222) reflection] is always fully excited, we consider as a source of phase information the small perturbations observed in azimuthal scans when the Ewald sphere is approaching one or two extra nodes in reciprocal space.

It has been observed in our laboratory that appreciable perturbations of the two-beam intensity, of the order of 5%, can be observed in azimuthal scans even when the angle φ is 2° off the value required for full excitation of one or more extra reflections. In this situation we introduce the notion of virtual Bragg scattering to point out the fact that the main reflection [for example, the (222) reflection in silicon] is perturbed by other Bragg reflections that cannot be excited because energy conservation would be violated. Figure 2 shows the experimental results along with our N-beam computations. A monochromatic beam (Cr $K\alpha$, $\lambda = 2.29$Å) impinges on a silicon perfect crystal, cut parallel to the (111) plane, set for diffracting the (222) reflection. It is well known that the (222) is exceedingly weak because it is forbidden and owes its existence to asphericity of bonding electrons.

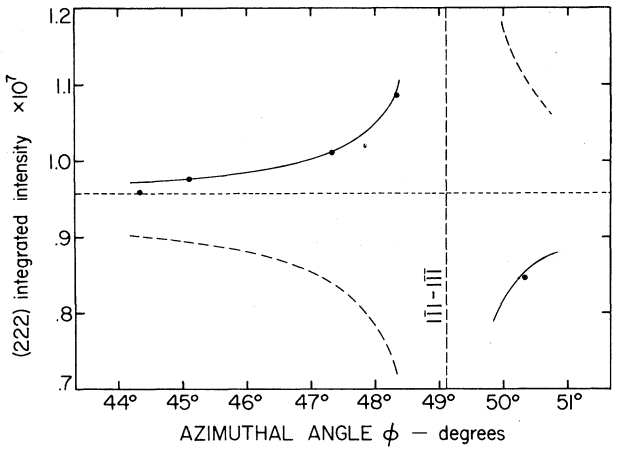

FIG. 2. Intensity of the (222) reflection as a function of azimuthal angle. Each point represents an integrated intensity with respect to θ, angle of incidence. Two strong umweg peaks, with angles 3′ apart, are located at a position marked by a vertical dotted line at $\varphi \cong 49.08'$. The two peak positions are not resolvable in this figure. Experimentally, one single peak is observed, 0.7° wide, with a peak intensity about a factor of 6.5 greater than the two-beam (222) value.

The region around $\varphi = 49°$ is explored in detail. There are two strong umweg peaks in this region, the $(1, \bar{1}, 1)$ at $\varphi = 49°06'$ and the $(1, \bar{1}, \bar{1})$ at $\varphi = 49°09'$.[7] Each experimental point in Fig. 2 corresponds to an integrated intensity with respect to θ, the angle of incidence. The statistical accuracy of each point is ±0.2%. The solid curve represents a four-beam calculation based on the theory and the computational procedures described in Ref. 5. Each point of the solid curve represents an integrated intensity, with respect to θ, of the computed profile, while φ is held constant. An important approximation is involved in this step. The calculations are carried out under the assumption of a plane wave, that is to say, a perfectly parallel beam without vertical or horizontal divergence. In the experiment, however, the beam has a vertical divergence of about 0.7°, as shown by the experimental width of the (2, 2, 2) -$(1, \bar{1}, 1)$-$(1, \bar{1}, \bar{1})$ umweg peak. Since we are considering the tail of the peak, we can safely assume that the intensity varies more or less linearly within the azimuthal "window" $\Delta\varphi (\simeq 0.7°)$, so that a point for a specific value φ_0 is really an average over $\Delta\varphi$ and can be directly compared to the calculated value. In this way we do not need to perform a laborious two-dimensional integration (versus θ and φ) as would be required if we were to use the fully excited umweg peaks, for comparison between theory and experiment.[5] The theoretical and experimental values have been standardized by means of the two-beam values.

As can be seen, the agreement between theory and experiment is excellent. We emphasize that the mechanism responsible for appreciable deviations from the two-beam value at angles φ that are 2° or 3° off the umweg peaks is basically different from that involved in the tails of an ordinary two-beam diffraction peak. In the latter, momentum is not conserved, and the intensity falls off very rapidly with θ. In a typical two-beam diffraction peak the intensity falls to 5% of the maximum value at an angle $\theta \simeq 5'' - 10''$ off the peak value, which corresponds to a distance between the Ewald sphere and the (h, k, l) node of the order of 0.001% of the radius. It turns out that Δp_x and Δx, as calculated from dynamical theory (x is a direction normal to the surface and Δx is the penetration, i.e., the extinction length of the x-ray beam) satisfy the uncertainty principle $\Delta x \, \Delta p_x \simeq \hbar$.

In our experiment (Fig. 2) the main reflection, the (222) reflection, is always fully excited, so

that momentum is always conserved. The participating (h', k', l') nodes perturb the (222) intensity at large distances from the Ewald sphere. For example, at $\varphi = 45°06'$, which is 4° off the $(1, \bar{1}, 1)$ umweg peak, the (222) intensity is about 2% greater than the two-beam value, and the participating $(1, \bar{1}, 1)$ and $(1, \bar{1}, \bar{1})$ nodes have distances that are, respectively, 3.2% and 1.0% of the radius, which is enormous compared to the 0.001% we found in the two-beam case. We have, therefore, a situation in which Bragg reflections that cannot be excited because energy would not be conserved in the process are able to affect appreciably the (222) intensity. In this sense we introduce the notion of virtual Bragg scattering, in analogy with virtual transitions in atomic and nuclear physics that do not conserve energy. The deviations from the two-beam value observed in Fig. 2, positive on the left side of the umweg peaks and negative on the right side, *do contain phase information.* To check this point, we pretend for a moment that instead of silicon we are dealing with a centrosymmetric crystal with a different atomic arrangement within the Bravais cell. In a centrosymmetric crystal, the phases of all reflections can only be 0 or π rad.

It is conceivable that the "new" crystal we are dealing with has the same structure factors as silicon except that one of the structure factors —for example, the one for the $(1, \bar{1}, \bar{1})$ node—has a different sign. This different sign has well recognizable effects on the calculated intensities. In this case the dotted curve is obtained in Fig. 2. The sign of the asymmetry is now reversed. By comparing our experimental points with the two sets of calculated curves (dotted and solid lines), the phase identification of the $(1, \bar{1}, \bar{1})$ node is unmistakable.

We believe that this method of phase identification based on virtual Bragg scattering has a far greater range of applicability than the methods described in Refs. 5 and 6. For one thing, a double integration is not needed in the computations, which drastically reduces computing time.

More importantly, we propose that this method can be applied to mosaic crystals, the ones for which real phase problems do exist. Our assumption can be justified by the following considerations. It is well known that dynamical and kinematical theory converge to the same results for very weak reflections. This is shown to be mathematically true, for example, in the Bragg case of diffraction,[8] and it is true in general. The physical reason for this convergence of the two theories is that dynamical theory implies multiple scattering in a crystal which is spatially coherent over long distances (centimeters) whereas kinematical theory assumes single-scattering processes. When the interaction between a photon and a crystal is very weak, the photon will most likely be scattered only once, even in a perfect crystal.

This is exactly the situation of our experiment. The primary reflection, the (222) reflection, is very weak and therefore is entirely kinematic. Other strong reflections are involved, but are weakly excited as a consequence of a proper choice of the azimuthal angle φ. Within each mosaic grain the scattering mechanism is that of a perfect crystal. What makes the difference between a perfect and a mosaic crystal is the possibility of multiple-scattering events at distances exceeding the average size of a mosaic block. Such processes are likely to happen when the scattering is strong and the crystal is perfect. If, however, the scattering is weak, or the blocks are randomly misoriented, multiple scattering over distances greater than the average dimension of a mosaic block does not happen, and the scattering mechanism in a perfect crystal, in the two-beam as well as in the N-beam case, becomes indistinguishable from that operating in a mosaic crystal.[9,10]

In our experiment, the overall interaction between x-ray photons and crystal is very weak; therefore crystal perfection should not play any role in the diffracted intensities.

We therefore believe that the method is directly applicable to mosaic crystals, and offers a practical solution to the phase problem.

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[1]W. N. Lipscomb, Acta Crystallogr. 2, 193 (1949).

[2]I. Fankuchen and H. Ekstein, private communication to Lipscomb, Ref. 1.

[3]M. Hart and A. R. Lang, Phys. Rev. Lett. 7, 120 (1961).

[4]H. Cole, F. W. Chambers, and H. M. Dunn, Acta Crystollogr. 15, 138 (1962).

[5]R. Colella, Acta Crystallogr. Sect. A 30, 413 (1974).

[6]B. Post, Phys. Rev. Lett. 39, 760 (1977).

[7]The zero on the φ scale corresponds to the [1$\bar{1}$0] direction lying on the diffraction plane.

[8]P. B. Hirsch and G. N. Ramachandran, Acta Crystallogr. 3, 187 (1950).

[9]In electron diffraction, "virtural Bragg scattering" is a common occurrence and must be always taken into account in quantitative experiments. See, for example, F. Fujimoto, J. Phys. Soc. Jpn. 15, 1022 (1960), on the (222) reflection in silicon.

[10]The need of using a dynamical N-beam diffraction theory for imperfect crystals was pointed out by M. Kuriyama, Acta Crystallogr. Sect. A 25, 56 (1969).

Domain Growth of Degenerate Phases

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The domain-coarsening kinetics of ordering systems with p-fold–degenerate equilibrium states, quenched from high temperatures, is analyzed. For long times (t) and low temperatures, the domain sizes equilibrate as a power law in t for $p < d+1$ and as a logarithmic function of t for $p \geq d+1$, where d is the spatial dimensionality of the system. The relation of these slowly equilibrating, kinetically disordered systems to glasses and suggestions for simulations and experiments are discussed.

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The structures of charge-density–wave systems,[1] adsorbed atoms on surfaces,[2] some intercalation compounds,[3] ordering alloys,[4,5] and antiferromagnets[6,7] are all characterized by a discrete number of low-temperature phases which are thermodynamically degenerate. For example, certain ordered phases of rare-gas atoms on the surface of Grafoil consist of three equivalent sublattices (degeneracy $p=3$), whose thermodynamics is derived from a Hamiltonian of the three-state Potts model.[2] Recent Monte Carlo calculations of the approach to equilibrium of ordering alloys and magnets quenched from high temperatures have indicated that, for spatial dimensionality $d=3$, systems with twofold-degenerate low-temperature equilibrium phases ($p=2$) do approach equilibrium as expected, with large domains of equivalent phases.[6] However, the four-state antiferromagnetic Potts model[7] in $d=3$, as well as[8,9] the three-state ferromagnetic Potts model ($p=3$) for $d=2$, has been reported[7-9] to maintain some of their quenched-in disorder for quenches from high to low temperatures. This phenomenon is reminiscent of descriptions of glasses[10] and is in agreement with a discussion by Lifshitz[11] of the difficulty of equilibrating systems with $p \geq d+1$.

This paper is a first step in establishing a quantitative basis for this suggestion by Lifshitz,[11] using a time-dependent Ginzburg-Landau approach[12,13] to calculate the domain-growth rate for various values of d and p. The equilibration of systems with $p \geq d+1$ is shown to be frustrated and hence characterized by a domain size which grows only logarithmically in time. While some of the arguments given here are independent of the details of any particular system, it is useful to consider a specific model. For example, the three-state Potts model[14] represents a system where each lattice site is characterized by a spin which can have three possible values. The order parameter consists of an amplitude ρ and a phase η.[14] For fixed ρ, the free energy is minimized by uniform, degenerate phases with $\eta=0$ and $\pm\frac{2}{3}\pi$ representing the three possible spin values. For long times after a quench from a high-temperature (T) disordered phase ($\rho=0$), it is expected that the system is uniformly characterized by its equilibrium value of $\rho_0(T)$ and by a spatially nonuniform $\eta(\vec{r})$, describing the arrangement of microdomains whose characteristic size is much greater than that of a lattice constant, but much smaller than that of the sample.[15]

For uniform $\rho=\rho_0(T)$, the free-energy density $F(\vec{r})$ can be written[14] in a continuum approximation as

$$F = F_0 - \tfrac{1}{3}b\cos 3\eta\rho_0^3 + \tfrac{1}{2}c\rho_0^2|\nabla\eta|^2, \quad (1)$$

where b and d are positive constants and where F_0 is the free energy of the uniform, single-domain system. Rescaling the energy by $b\rho_0^3$, the length by $(c/b\rho_0)^{1/2}$, and generalizing to p-fold–degenerate systems, the time dependence of η is