Distortion and Peak Broadening in Quasicrystal Diffraction Patterns

T. C. Lubensky, Joshua E. S. Socolar, Paul J. Steinhardt, Peter A. Bancel, and Paul A. Heiney
Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania 19104
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In this paper, we discuss how quenched strains in phonon and phason variables and/or quenched dislocations can lead to peak broadening and distortion in quasicrystal diffraction patterns. We argue that high-resolution electron micrographs and observations of distortions in electron diffraction patterns indicate the presence of anisotropic strains in the phason variable in the icosahedral phase of Al-Mn and related alloys. Such strains also contribute to the x-ray peak widths and line shapes.

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Recently, an "icosahedral phase" which diffracts electrons in an icosahedrally symmetric pattern consisting of rather sharp spots has been observed in rapidly cooled aluminum-manganese and related alloys.[1] The icosahedral quasicrystal[2] (IQ), a structure characterized by long-range quasiperiodic translational order and icosahedral orientational order, is a leading model for this new phase. An ideal IQ has an icosahedrally symmetric diffraction pattern consisting of true Bragg peaks with positions and intensities in rough agreement with the electron diffraction observations of the icosahedral phase. Subsequent experiments have revealed some systematic deviations from the ideal quasicrystal model: High-resolution x-ray powder diffraction studies of the icosahedral phase[3] show a broadening of peaks which does not increase uniformly with scattering angle, and recent electron-diffraction observations of the icosahedral phase in melt-spun Al-Mn and related alloys indicate anisotropic peak broadening and subtle distortion of the diffraction pattern as a whole.[4,5]

The purpose of this paper is to provide a simple theoretical explanation for these and other observations. We shall point out how strains in phonon and phason variables or quenched dislocations[6] can lead to peak broadening and distortion[7] in diffraction patterns. We shall present evidence for quenched anisotropic phason strains in high-resolution electron micrographs and in recent electron-diffraction observations of single grains. We suggest that strains may also account for the finite peak widths and line shapes in x-ray powder diffraction studies which correspond to an angular and ensemble average over many grains.

The broken-symmetry hydrodynamic variables[8,9] for an IQ can be expressed in the form of two three-dimensional vectors: a translation vector $\mathbf{u}$ (which also occurs for crystals), and a phason vector $\mathbf{w}$ (which does not). The mass density of an ideal IQ can be expressed as a sum of mass-density waves whose amplitudes have magnitudes $|\rho_{\mathbf{G}}|$ and phases $\phi_{\mathbf{G}}$ where $\mathbf{G}$ is a vector in the reciprocal lattice L_R. Spatially uniform shifts, $\Delta\mathbf{u}$ and $\Delta\mathbf{w}$, do not change amplitudes of the density waves but do change phases: $\Delta\phi_{\mathbf{G}}=\mathbf{G}\cdot\Delta\mathbf{u}+\bar{\mathbf{G}}\cdot\Delta\mathbf{w}$. $\bar{\mathbf{G}}$ is defined as follows: Any $\mathbf{G}$ in L_R can be expressed as $\sum_{k=0}^{5}n_k\mathbf{G}_k$, where each n_k is an integer and each $\mathbf{G}_k$ is an icosahedral vertex vector; $\mathbf{G}_5=(0,0,1)$ and $\mathbf{G}_k=[\sin\beta\cos(2\pi k/5),\ \sin\beta\times\sin(2\pi k/5),\cos\beta]$ for $k=0,\ldots,4$, where $\cos\beta=1/\sqrt{5}$. In terms of this set of n_k's, $\bar{\mathbf{G}}\equiv\sum_{k=0}^{5}n_k\mathbf{G}_{\langle 2k\rangle}$, where $\mathbf{G}_{\langle 2k\rangle}$ is $\mathbf{G}_{2k\,(\mathrm{mod}\,5)}$ for $k\leq 4$ and $-\mathbf{G}_5$ for $k=5$.[10]

The density-wave amplitudes may be viewed as the order parameters for the IQ phase. Thermal fluctuations and quenched spatial variations in $\mathbf{u}$ and $\mathbf{w}$ can then be described in terms of spatially varying $|\rho_{\mathbf{G}}(\mathbf{x})|$ and $\phi_{\mathbf{G}}(\mathbf{x})$. The thermally averaged mass density is, therefore,

$$\langle\rho(\mathbf{x})\rangle=\sum_{\mathbf{G}\in L_R}\langle\rho_{\mathbf{G}}(\mathbf{x})\rangle\exp(i\mathbf{G}\cdot\mathbf{x}),\tag{1}$$

where the angular brackets denote thermal average and $\rho_{\mathbf{G}}(\mathbf{x})\equiv|\rho_{\mathbf{G}}(\mathbf{x})|\exp[i\phi_{\mathbf{G}}(\mathbf{x})]$.

In a scattering experiment, the measured intensity at momentum transfer $\mathbf{q}$ is proportional to

$$I(\mathbf{q})\equiv\int d^3x\,d^3x'\langle\rho(\mathbf{x})\rho(\mathbf{x}')\rangle\exp\{-i\mathbf{q}\cdot(\mathbf{x}-\mathbf{x}')\}.\tag{2}$$

In systems with long-range periodic or quasiperiodic order, $I(\mathbf{q})$ is dominated by coherent scattering in Bragg peaks at wave vector $\mathbf{G}$:

$$I(\mathbf{q})\approx\int d^3x\,d^3x'\exp\{-i\mathbf{q}\cdot(\mathbf{x}-\mathbf{x}')\}\langle\rho(\mathbf{x})\rangle\langle\rho(\mathbf{x}')\rangle=V^2\sum_{G\in L_R}|\langle\rho_{\mathbf{G}}(\mathbf{x})\rangle|^2\delta_{\mathbf{q},\mathbf{G}},\tag{3}$$

where V is the volume. In thermal equilibrium, $\langle\rho_{\mathbf{G}}(\mathbf{x})\rangle=\langle\rho_{\mathbf{G}}\rangle$ is independent of $\mathbf{x}$. Thermal fluctuations in $\mathbf{u}$

and $\mathbf{w}$ reduce the magnitude $\langle\rho_{\mathbf{G}}\rangle$ via a generalized Debye-Waller factor,[11] $|\langle\rho_{\mathbf{G}}\rangle| \approx \langle|\rho_{\mathbf{G}}|\rangle \exp(-W_{\mathbf{G}})$, where $W_{\mathbf{G}} = \frac{1}{2}\langle[\mathbf{G}\cdot\mathbf{u}(\mathbf{x}) + \mathbf{G}\cdot\mathbf{w}(\mathbf{x})]^2\rangle$, but do not induce broadening of the peaks or shifts in their positions.

The hydrodynamic theory for the IQ predicts that $\mathbf{u}$ relaxes rapidly via phonon modes, whereas $\mathbf{w}$ relaxes diffusively with relaxation times that are estimated to be extremely long.[8] This suggests that variations in $\mathbf{w}$ present just after the rapid solidification of the IQ phase may remain essentially constant or "quenched" throughout the time period of any laboratory experiment. Other variables, such as $\mathbf{u}$, will relax quickly to their equilibrium values in the presence of the quenched field, $\tilde{\mathbf{w}}(\mathbf{x})$. Experiments, therefore, measure expectation values in the presence of a quenched background field, $\tilde{\mathbf{w}}(\mathbf{x})$. We will denote these expectation values by $\langle\ \rangle_{\mathbf{w}}$. The density-wave amplitudes are then given by

$$\langle\rho_{\mathbf{G}}(\mathbf{x})\rangle_{\mathbf{w}} = |\langle\rho_{\mathbf{G}}\rangle| \exp\{i[\mathbf{G}\cdot\tilde{\mathbf{u}}(\mathbf{x}) + \bar{\mathbf{G}}\cdot\tilde{\mathbf{w}}(\mathbf{x})]\}, \tag{4}$$

where $\tilde{\mathbf{u}}(\mathbf{x})$ is the equilibrium value of $\mathbf{u}$ induced by the elastic coupling of $\mathbf{u}$ to $\tilde{\mathbf{w}}$, as described by the elasticity theory.[8] Let us first consider the case in which there is no elastic coupling between $\mathbf{u}$ and $\mathbf{w}$ (i.e., spatial variations only in $\mathbf{w}$).

If the spatial variations in $\mathbf{w}$ are approximately linear over the scattering volume or over a given microcrystal, then we can write $\mathbf{w} = \mathbf{M}\cdot\mathbf{x}$, where $\mathbf{M}$ is a second rank tensor, and, from Eqs. (4), (1), and (3), we find

$$I(\mathbf{q}) \approx \int d^3x\, d^3x' \langle\rho(\mathbf{x})\rangle_{\mathbf{w}}\langle\rho(\mathbf{x}')\rangle_{\mathbf{w}} \exp\{-i\mathbf{q}\cdot(\mathbf{x}-\mathbf{x}')\} = V^2 \sum_{\mathbf{G}\in L_R} |\langle\rho_{\mathbf{G}}\rangle|^2 \delta_{\mathbf{q},\mathbf{G}+\Delta\mathbf{G}}, \tag{5}$$

where $\Delta\mathbf{G} = \bar{\mathbf{G}}\cdot\mathbf{M}$. Thus, a quenched linear strain in $\mathbf{w}$ anisotropcally shifts the Bragg peaks by an amount proportional to $|\bar{\mathbf{G}}|$ rather than $|\mathbf{G}|$.[7] This is in contrast to the situation of a uniform compression or shear (a variation of $\mathbf{u}$) in a crystal or quasicrystal where peak shifts are proportional to $|\mathbf{G}|$, leading to a compression or shear of the entire reciprocal lattice itself. Linear strains in $\mathbf{w}$ will transform a set of diffraction peaks which lie symmetrically about a circle of constant $|\mathbf{q}|$ into a set in which $|\mathbf{q}|$ varies about the ideal positions in proportion to $|\bar{\mathbf{G}}|$, anisotropically distorting the circle of peaks. Since the peak intensities in an ideal IQ tend to fall off with increasing $|\bar{\mathbf{G}}|$, circles containing less intense peaks exhibit greater distortion. In Fig. 1 we illustrate the effect of a such linear $\mathbf{w}$ strain on the IQ fivefold diffraction pattern. A $\mathbf{w}$ strain that varies quadratically or with some higher power of $\mathbf{x}$ will produce an anisotropic peak broadening in addition. A pure sinusoidal variation in $\mathbf{w}$ strain produces a sequence of narrowly spaced satellite peaks about each original peak; a distribution of such strains would appear as an effective broadening in diffraction measurements.

We have also considered the limit of a quenched "random" $\tilde{\mathbf{w}}(\mathbf{x})$ (i.e., one whose Fourier components are independent random variables). X-ray powder diffraction experiments effectively average over the possible realizations of $\tilde{\mathbf{w}}$. For simplicity, we will restrict our discussion to spatially isotropic distributions for which $[\tilde{\mathbf{w}}^2(\mathbf{x})] \sim L^{\alpha} + \text{const}$ and $[\{\tilde{\mathbf{w}}(\mathbf{x}) - \tilde{\mathbf{w}}(0)\}^2] \sim |\mathbf{x}|^{\alpha} + \text{const}$, where the square brackets denote average over $\tilde{\mathbf{w}}$ and L is the length of the sample. The scattering intensity is then given by

$$I(\mathbf{q}) \approx \int d^3x\, d^3x' [\langle\rho(\mathbf{x})\rangle_{\mathbf{w}}\langle\rho(\mathbf{x}')\rangle_{\mathbf{w}}] \exp\{-i\mathbf{q}\cdot(\mathbf{x}-\mathbf{x}')\}. \tag{6}$$

In analogy with the discussion of Eqs. (3) and (4), we first consider

$$[\langle\rho_{\mathbf{G}}(\mathbf{x})\rangle_{\mathbf{w}}] = |\langle\rho_{\mathbf{G}}\rangle| \exp\{-\tfrac{1}{2}\bar{\mathbf{G}}^2[\tilde{\mathbf{w}}^2(\mathbf{x})]\}$$

(where we have used the assumption that the distribution of $\tilde{\mathbf{w}}$ is isotropic). If $[\langle\rho_{\mathbf{G}}(\mathbf{x})\rangle_{\mathbf{w}}]$ is nonzero (i.e., $[\tilde{\mathbf{w}}^2(\mathbf{x})]$ remains finite at large L or, equivalently, $\alpha < 0$), the Bragg peaks will remain and $I(\mathbf{q})$ is given by an expression similar to Eq. (3), except with the thermal average replaced by the quench average; the result is a quench-averaged rather than a thermal-averaged Debye-Waller factor. (There will be additional diffuse background scattering in this situation.) That is, the Bragg peaks persist if slow (long wavelength) spatial variations are not too heavily weighted in the quench average. If, on the other hand, $[\tilde{\mathbf{w}}^2(\mathbf{x})] \to \infty$ as $L \to \infty$ ($\alpha > 0$), the Bragg peaks are destroyed by the average over $\tilde{\mathbf{w}}$. Broadened peaks can remain, however. Equation (6) reduces to

$$I(\mathbf{q}) = \int d^3x \sum_{\mathbf{G}\in L_R} |\langle\rho_{\mathbf{G}}\rangle|^2 \exp(-i(\mathbf{q}-\mathbf{G})\cdot\mathbf{x} - \tfrac{1}{2}\bar{\mathbf{G}}^2[\{\tilde{\mathbf{w}}(\mathbf{x}) - \tilde{\mathbf{w}}(0)\}^2]). \tag{7}$$

The shapes of the broadened peaks depend on the value of α. For $\alpha \to 0$, the peaks have a power-law divergence similar to those for a smectic liquid crystal. For $\alpha = 1$, the peaks have Lorentzian-squared shape with widths proportional to $\bar{\mathbf{G}}^2$. For $\alpha = 2$, the peaks are Gaussian with widths proportional to $|\bar{\mathbf{G}}|$. In all cases, the peak widths increase monotonically with $|\bar{\mathbf{G}}|$.

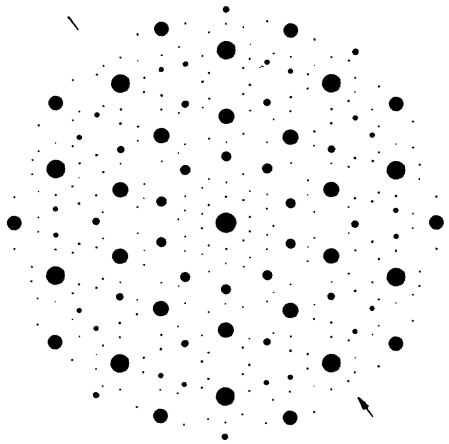

FIG. 1. A distorted diffraction pattern due to anisotropic linear strain in **w**. The peaks remain true Bragg peaks (area of spots represents relative intensity). In an ideal quasicrystal, the peaks lie along straight lines. Hold at grazing angle and sight along narrow to observe the distortion of the pattern.

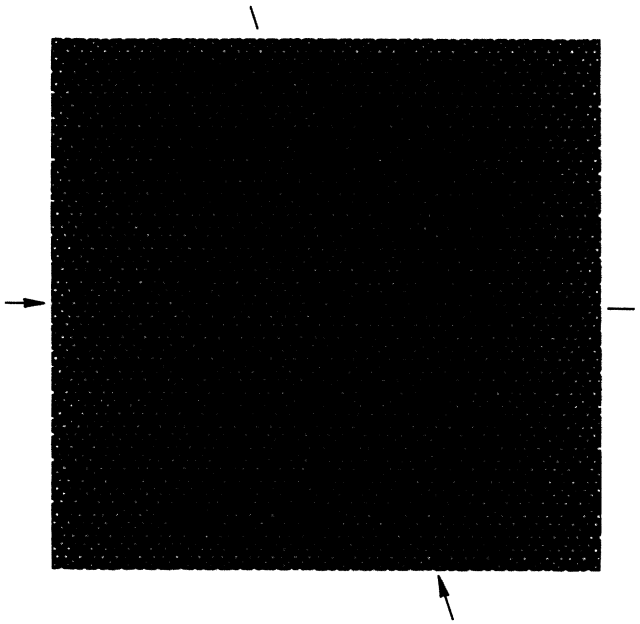

FIG. 2. A density-wave image obtained by summing of five pentagonally oriented density waves. A linear strain in **w** has been introduced along the vertical direction. White regions represent densities greater than $\frac{2}{5}$ maximum density. The arrow on the left-hand side points along a straight line of white regions, as occurs in the ideal quasicrystal. The arrow on the lower right-hand side points to a line of white regions that occasionally jags. Compare with the high-resolution micrographs found in Ref. 14.

The elastic energy[8] of the IQ has terms coupling gradients in **u** to gradients in **w**. Thus, a quenched, spatially varying **w** acts as a source to create a spatially varying **u**. In principle, there should be shifts and broadening of peaks arising from the induced variations in **u** whose effect should increase monotonically with **G**, rather than $\overline{\mathbf{G}}$. Finally, we note that dislocations carry both **u** and **w** variations. Dislocations, if they are present, will have difficulty annihilating and relaxing because of the **w** field and will be effectively quenched. Thus, even if the **u**-**w** coupling is small, isolated dislocations will produce **u** strains and contribute a **G**- (as well as $\overline{\mathbf{G}}$) dependent broadening of diffraction spots. These effects may contribute to nonmonotonic behavior of linewidths as a function of $\overline{\mathbf{G}}$.

Having discussed the effects of quenched **w** strain from a theoretical point of view, we now wish to present some evidence for their presence in icosahedral alloys.

(a) High-resolution electron micrographs obtained by imaging (Fourier transformation) of the fivefold diffraction of IQ's exhibit **w** strain but not **u** strain.[12] The micrograph can be directly compared to images formed by adding five pentagonally oriented density waves in the plane, as in Fig. 2. In the ideal structure, the density maxima (indicated by the white dots in the figure) lie along quasiperiodically spaced straight lines oriented along pentagonal symmetry directions. Hiraga *et al.*[13] show that the **u** strains introduce curvature in the lines, whereas **w** strains maintain straight lines but introduce "jags"—one line of high-density points stops and another, shifted by a discrete distance, begins. In Fig. 2, only **w** strain has been imposed, leading to a set of jagged straight lines. In our observations of several high-resolution micrographs published in the literature,[13] we find that nearly all micrographs show evidence of jags, but there is no evidence of curvature. This observation is consistent with the hypothesis that there is a quenched **w** strain and that the **u**-**w** elastic coupling is weak. From these data alone, however, it is difficult to determine whether the **w** variation is random or anisotropic.

(b) Recent electron-diffraction experiments[3,5] on the icosahedral phases of Al-Mn, Al-Mn-Si, and Al-Cr-Ru indicate that there are systematic distortions in the diffraction patterns. Similar distortions are seen in essentially all samples, although the magnitude of the distortion varies from sample to sample. In Fig. 3, an electron-diffraction pattern is shown for the fivefold symmetry axis of the icosahedral phase of $Al_{78}Cr_{17}Ru_5$ in which one can detect the same $|\overline{\mathbf{G}}|$-dependent distortion as illustrated in Fig. 1, strongly suggesting that significant *anisotropic* **w** *strains* are quenched in the grains. Many of the electron diffraction patterns also reveal an *anisotropic broadening* (elongation) of the electron-diffraction peaks, characteristic of a quenched **w** strain which varies nonlinearly with position.

(c) One of the major challenges to the quasicrystal model has been to explain the finite peak widths found

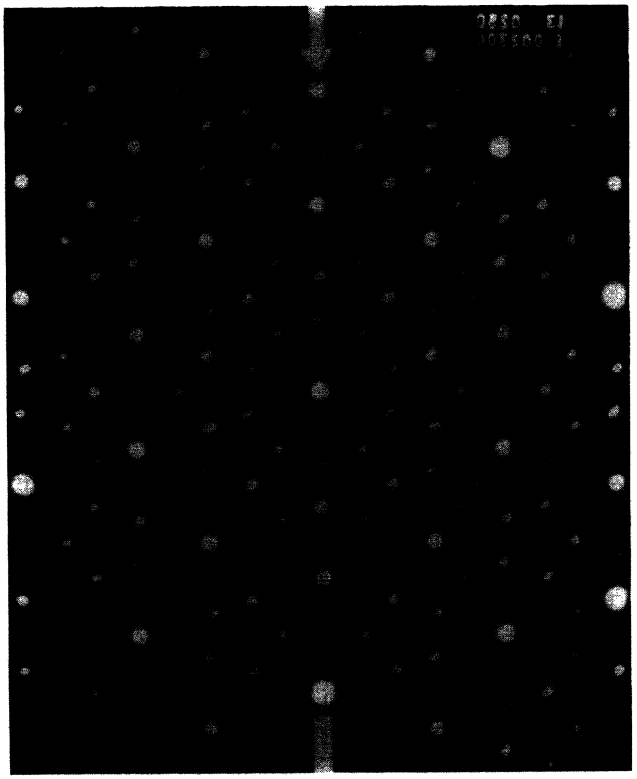

FIG. 3. An electron diffraction pattern in a fivefold symmetry plane of the icosahedral phase of $Al_{78}Cr_{17}Ru_5$ which shows particularly large anisotropic shifts in the peak positions similar to Fig. 1. Also note the anisotropic broadening of the individual peaks.

in the powder-averaged x-ray diffraction measurements.[4] We now see that there are two natural explanations for the finite peak widths within the quasicrystal model: (1) random isotropic quenched **w** strains (or dislocations), and (2) anisotropic quenched **w** strains. Effect (1) produces an *intrinsic broadening* of every peak (symmetrical in $|\mathbf{q}|$), and thus leads to a broadening in the powder-averaged x-ray peaks. Effect (2) produces peak broadening in two ways. First, to the extent that it produces an intrinsic anisotropic broadening of each peak, it will also lead to a broadening of the powder-averaged x-ray peaks. Secondly, anisotropic **w** strains shift the $|\mathbf{q}|$ associated with the peaks, so that peaks with the same $|\mathbf{q}|$ in an ideal quasicrystal are now separated in $|\mathbf{q}|$ in proportion to $|\bar{\mathbf{G}}|$. Even if there were no intrinsic broadening of the peaks at all, this last effect would produce an *induced broadening* in the x-ray powder-diffraction experiments since they measure $|\mathbf{q}|$ only. At present, the degree to which the peak widths measured in x-ray diffraction increase monotonically with $|\bar{\mathbf{G}}|$ varies significantly from sample to sample,[5] although it has been claimed that near monotonicity is found in the best annealed samples.[6] Even in the best samples that we have seen, there appears to be evidence of combined $|\bar{\mathbf{G}}|$ and $|\mathbf{G}|$ dependence. This could be due to the nonzero **u-w** elastic coupling or to the presence of isolated dislocations. We should also emphasize that any other effects producing quenched variations in **u**, such as variations in composition, can also produce **G**-dependent shifts and broadening. Careful measurements of the line shape and the variation of peak width with $\bar{\mathbf{G}}$ may lead to an understanding of the nature and source of **w** strains. Finally, we note that effect (2) can lead to asymmetrical broadening of the peaks in the x-ray powder diffraction experiments.[14]

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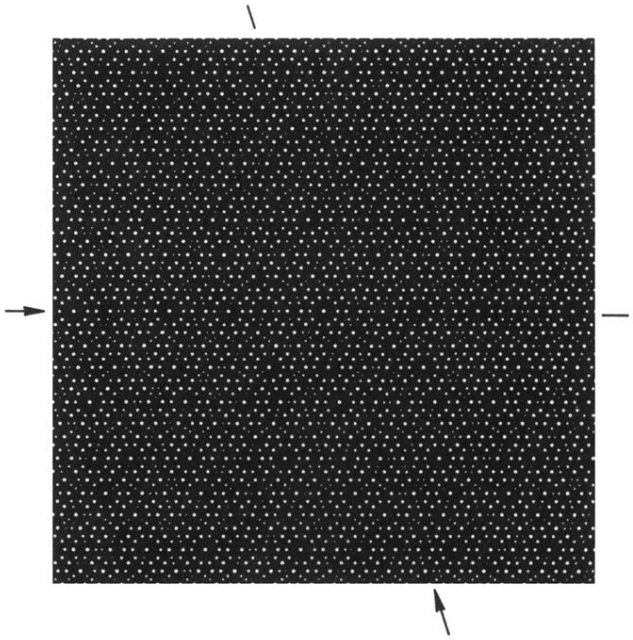

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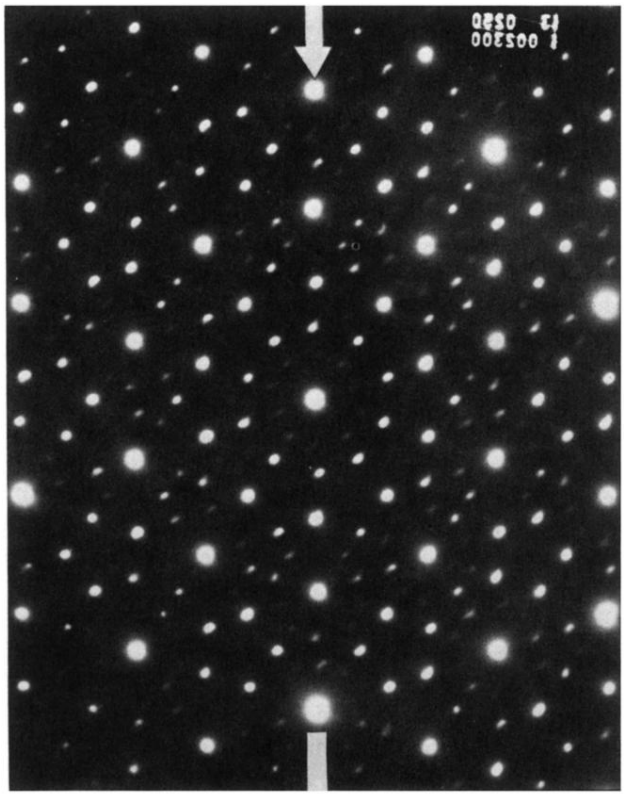

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