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Acta Cryst. (1973). **A29**, 710

Periodicity in Thickness of Electron-Microscope Crystal-Lattice Images

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(Received 24 April 1973; accepted 12 June 1973)

High-resolution electron micrographs of crystal lattices showing a recognizable correlation of intensity with atom positions are normally obtained only for very thin crystals (less than about 100 Å thick). For some crystals of niobium and titanium–niobium oxides, it has been observed that this thin-crystal contrast is repeated for thicknesses of the order of 1000 Å. This is regarded as evidence that under conditions of high symmetry of excitation, the wave field in the crystal is essentially periodic with distance in the beam direction if a particular relationship exists between the structure amplitudes and the excitation errors for the diffraction process. This is confirmed by calculations made for f.c.c. lattices with Cu, CuAu₃, or Au atoms and for a range of wavelengths.

Introduction

It has been shown recently (Iijima, 1971) that, when a thin crystal is aligned so that the incident electron beam is parallel to a principal axis, high-resolution electron micrographs can be obtained which show a direct correlation between image intensity and the projection of the crystal structure. In this way the distribution of metal atoms in a number of oxide phases has been determined both for perfect crystal regions and for linear or planar faults in the structures (Iijima, 1972, 1973; Iijima & Allpress, 1973). The nature of the contrast observed can be understood semi-quantitatively by application of the phase-object approximation (Cowley & Iijima, 1972). It is observed that when the crystal thickness exceeds that for which the phase-object approximation is expected to be valid, namely about 100 Å for 100 keV electrons, the image contrast no longer shows any obvious relationship to the crystal structure. This may be associated with the onset of three-dimensional dynamical diffraction conditions under which the variations of the relative phases and amplitudes of the many diffracted waves are very complicated and, in general, show no apparent periodicity with increasing thickness. However, for a few special cases an almost exact repetition of the thin-crystal contrast has been observed for relatively large thicknesses suggesting a recurrence of very nearly the same relative amplitudes and phases of the diffracted beams.

Observations

Fig. 1 is part of an electron micrograph of a crystal of the high-temperature phase, *H*-Nb₂O₅. The incident beam is parallel (within 3×10^{-3} radians) to the short *b* axis ($b = 3.8$ Å) of the monoclinic unit cell ($a = 21.2$, $c = 19.4$ Å, $\beta = 120^\circ$) and the image is obtained with approximately the 'optimum defocus' for phase contrast, $\Delta f = -900$ Å, using a modified JEM-100B electron microscope with a goniometer stage. Thickness determinations of the crystal were made by the observation of the images of planar faults for various tilts of the crystal. The crystal is wedge-shaped with an almost linear increase in thickness.

In the thin part of the crystal, near the edge of the wedge, the lattice image clearly shows the configuration of metal atoms within the unit cell which includes 4×3 and 5×3 blocks of ReO₃-type corner-sharing octahedra, plus atoms in tetrahedral positions which generate the darkest spots. A detailed study of the lattice images of *H*-Nb₂O₅ in both ordered and disordered forms has been reported by Iijima (1973) (see also Anderson, Browne & Hutchinson, 1972). With increasing crystal thickness this readily interpreted form of the image is lost for thicknesses of 100–150 Å and is replaced by a variety of image forms, none of which has any obvious relationship to the structure. Then for thicknesses of about 500 to 800 Å the thin-crystal image reappears with much the same contrast as for

the 0 to 100 Å range. Fig. 2 shows a small part of the thick-crystal region, reproduced with higher magnification. It is seen that the perfect crystal regions and the crystal defects are equally well imaged.

The same phenomenon of a repetition of the thin-crystal contrast has been observed for Nb₁₂O₂₉ (orthorhombic, $a=20.5$, $b=3.8$, $c=15.6$ Å), for TiNb₂₄O₆₂ ($a=29.8$, $b=3.8$, $c=21.1$ Å), viewed with the incident beam parallel to the b -axis, and for the orthorhombic form of Ti₂Nb₁₀O₂₉ (Iijima, 1971). But no such repetition has been detected for the oxide structures related to the tetragonal tungsten bronze structure (Iijima, 1972), namely 4Nb₂O₅.9WO₃ ($a=12.9$, $b=3.8$, $c=36.7$ Å) and 2Nb₂O₅.7WO₃ ($a=c=24.3$, $b=3.8$ Å), or for a variety of other materials which have been examined.

For the niobium and niobium-titanium oxides, attempts were made to detect a second repetition of the thin-crystal contrast for thicknesses of the order of 2000 Å but no definite result could be obtained partly because absorption rendered the images too weak for convenient observation and partly because for thicker regions the requirements for alignment of the crystals may be expected to be even more exacting. A further observation is that the general level of intensity in the images shows damped oscillation with thickness corresponding to the variation of the incident beam intensity. The good images are seen to recur on the higher-thickness side of a bright part of the image, *i.e.* where the incident beam is much stronger than the diffracted beams and is decreasing, as in the thin-crystal region.

Analogous theoretical results

The implication of these observations is that under the conditions of high symmetry of excitation by an incident beam parallel to a principal axis, the electron wave function in some particular crystals shows an apparent periodicity in the beam direction. The relative amplitudes of all diffracted beams should then show periodicity with crystal thickness.

This is reminiscent of the results of Fisher (1968) who made N -beam dynamical calculations of the intensities given by a hypothetical disordered CuAu₃ alloy (assuming $\frac{3}{4}$ Au + $\frac{1}{4}$ Cu at each lattice site of a f.c.c. structure and neglecting absorption) for the incident beam exactly parallel to the [001] axis. He found the intensity of all diffracted beams to vary sinusoidally with thickness, all with the same periodicity. The non-zero-order beam intensities varied exactly in phase with each other and exactly out of phase with the zero-order beam. A re-calculation of his results for 100 keV electrons is plotted in Fig. 3(c). Following Fisher, the calculation was made using the beam-reduction technique possible because of the high symmetry of the diffraction pattern. The curves for the diffracted beam intensities are for, in decreasing order of intensity, one of the 200-type beams, one of the 220-type and one of the 400-type beams. The results differ in detail from those

of Fisher owing to the use of different atomic scattering amplitudes and Debye-Waller factors but they show the same apparently sinusoidal variation of the intensities and hence, presumably, of the relative amplitudes of the diffracted beams.

For diffraction from other face-centered cubic materials the same sinusoidal variation does not occur.

The parameters entering into the solution of the dynamic diffraction equations are the structure amplitudes and the excitation errors. It seems probable that the occurrence of an exact sinusoidal periodicity (or a close approximation to it) in the solution depends on some particular relationship between these parameters. We have confirmed this conclusion by making calculations in which these parameters were varied independently. Thus for Fig. 3(a) and (e) the structure amplitudes are varied by replacing the average CuAu₃ atoms by Cu and Au atoms respectively, with no variation of the lattice constant, $a=3.98$ Å, or wavelength. For Fig. 3(b) and (d) the excitation errors only are varied by assuming the wavelengths for 25 keV and 100 keV electrons instead of 100 keV. In each case the change introduces perturbations of the ideal sinusoidal behaviors of Fig. 3(c), visible most clearly for the weaker diffracted beams.

Discussion

We have sought a general form for a relationship between structure amplitudes and excitation errors which would lead to periodicity in the solution of the dynamical equations but so far without success. The repetition may be related to the 'quasi-periodicities' discussed by Anstis, Lynch, Moodie & O'Keefe (1973).

The phenomenon may be described in a number of ways. For example, in terms of a Bloch wave formulation, the condition for identical periodicities of all beams is that the wave function should be completely dominated by two Bloch waves only. Table 1 shows that this is the case for CuAu₃ at 100 keV. The contributions to three Bloch waves are given for the strongest three effective beams of the symmetry-reduced formulation. The components of the third Bloch wave are, at the greatest, less than 4% of the components of the first two. For CuAu₃ at 25 keV the third Bloch wave has components up to 10% of the others. For Cu atoms at 100 keV this figure is 28 and for Au atoms at 100 keV it is 6%.

Table 1. Calculations for CuAu₃, 100 keV, [001] orientation

Beam	Amplitudes of Bloch wave components		
	Bloch wave #1	Bloch wave #2	Bloch wave #3
(0,0,0)	0.224	0.775	0.000
(2,0,0)	0.149	-0.156	0.004
(2,2,0)	0.106	-0.107	-0.004

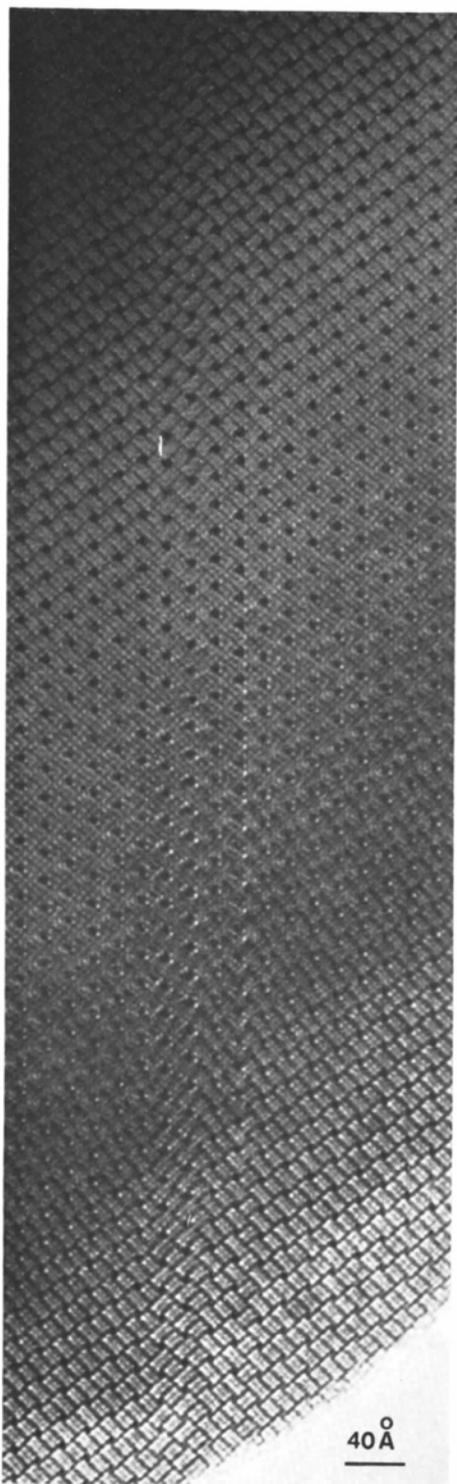


Fig. 1. Electron micrograph of wedge-shaped crystal of $H\text{-Nb}_2\text{O}_5$ with the incident beam parallel to the short b axis, defocused -900 Å. The image gives a direct representation of the projected crystal structure near the crystal edge (thicknesses up to ~ 100 Å) and again for relatively thick regions (approximately 500 to 800 Å).

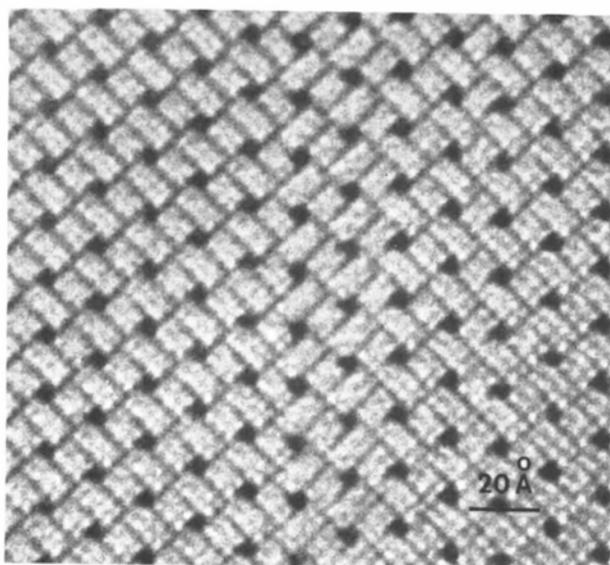


Fig. 2. Higher magnification of a thick-crystal part of Fig. 1 showing the distribution of metal atoms equally clearly in perfect and imperfect regions.

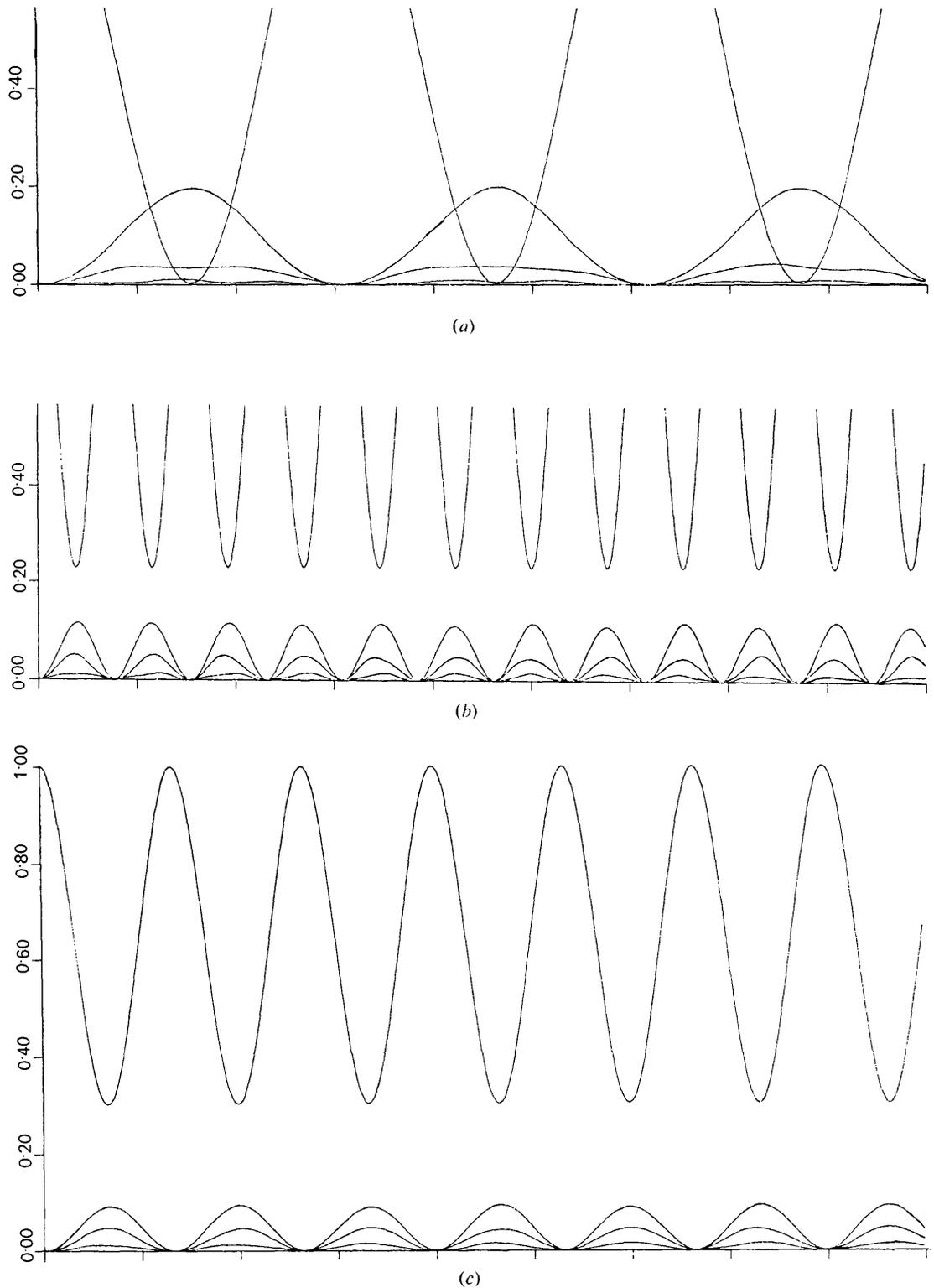


Fig. 3. Calculated intensities for diffracted beams given by a face-centered lattice, $a_0 = 3.98 \text{ \AA}$, with the incident beam exactly parallel to [001] assuming no absorption, (a) for Cu atoms, 100 keV; (b) for CuAu_3 (average) atoms, 25 keV; (c) for CuAu_3 , 100 keV; (d) for CuAu_3 , 1000 keV; (e) for Au atoms, 100 keV. For all curves except (c) the top half of the intensity has been omitted.

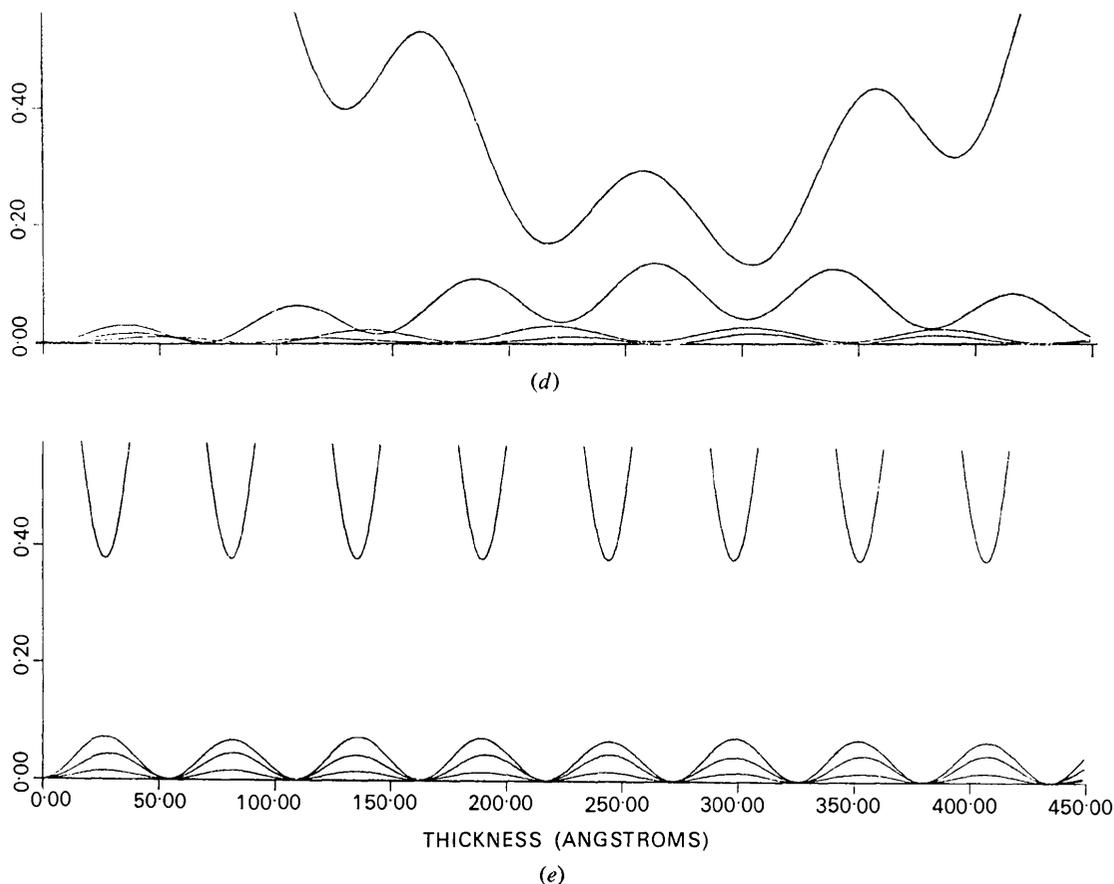


Fig. 3 (cont.)

In the case of the complicated oxide structures with large unit cells, it is more difficult to envision a simple relationship which would provide the condition for sinusoidal periodicity of the wave-field. The number of diffracted beams of appreciable amplitude is hundreds rather than the tens involved for simple face-centered cubic structures. The fact that the near-periodicity is observed for several structures having widely different unit-cell dimensions and symmetries suggests that the precise nature of the superlattice and the detailed distributions of the many diffracted beams are not relevant factors.

One significant observation in this regard is that, as seen in Fig. 2, the atoms around faults in the $H\text{-Nb}_2\text{O}_5$ structure are imaged as clearly as those in the perfect crystal areas for the large thickness region. This suggests that the dynamical scattering may be treated by use of a column approximation, *i.e.* that the intensity at any point in the image can be attributed to a column through the crystal of diameter not more than about 5 Å.

In each of these structures and in the defect regions the basic substructure unit is the square array of corner-sharing octahedra forming square tunnels through the

structure in the beam direction. The center of each of these tunnels is marked by a white dot in the thin-crystal image and it is the array of these white dots (excess intensity points) which forms the most noticeable and characteristic feature of the images. The recurrence of the image at greater thicknesses may be considered to be mainly due to a repetition of the thin-crystal wave function within these tunnels. The factors influencing this repetition are presumably the wavelength, the tunnel dimensions, and the average scattering power of the atoms surrounding the tunnel. For the tungsten bronze structures, which have not shown the repetition, both the tunnel dimensions and the average scattering power are different.

In terms of the diffraction pattern, the condition for repetition may be stated, equivalently, to be that strong groups of reflections should appear around positions corresponding to the sub-lattice periodicity and that the appropriate relationship should exist between the total scattered amplitudes and the average excitation errors for these groups.

The establishment of general guidelines which would suggest when the phenomenon of the repeated thin-crystal contrast might occur would be of obvious

