Moiré Patterns in Electron Diffraction from Lanthanum Oxide Iodide (LaOI)

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Abstract

Moiré interference effects have been observed in the electron diffraction patterns from crystals of lanthanum oxide iodide (LaOI). Optical transform methods were used to assist in the characterization of these patterns. The rotational misalignment of the overlapping pairs of thin crystals viewed in projection down [001] was found to take widely varying values. The higher values of the misalignment angle were found to occur close to the special values of tan⁻¹(1), tan⁻¹(1/2), tan⁻¹(2/3) etc. Patterns in which three different crystal orientations are overlapped have also been observed.

Moiré interference effects in thin crystalline materials have been observed in the electron microscope for many years. The definitive early work describing the phenomenon was by Bassett, Menter & Pashley (1958). Two distinct types of moiré pattern have been reported; either 'parallel' moirés caused by two aligned lattices of slightly different unit-cell size, or 'rotation' moirés produced by identical lattices with a rotational (usually small) misalignment. We have recently encountered some rather complex electron diffraction patterns, which we have been able to attribute to rotational moiré effects. In some cases the patterns observed have been found to be the result of the superposition of three different crystal orientations. Interpretation of the diffraction patterns was greatly aided by the use of optical transform techniques (Lipson, 1973) and provides an excellent example of how the use of such techniques can give a rapid and simple solution to quite complex diffraction problems.

The electron diffraction patterns, examples of which are shown in Figs. 1(a), (b) and (c), were first observed from impurity crystals in samples of LaVS₃ that had been synthesized from La₂S₃ and V₂S₃ using I₂ as a transporting agent. Oxygen was present as an impurity in the La₂S₃ starting material. Insufficient of the impurity material was present to allow its identification using X-rays. Following our interpretation of the diffraction patterns the impurity was subsequently identified as lanthanum oxide iodide (LaOI). In confirmation of this, pure LaOI was prepared by the method of Brown, Hall, Hurtgen & Moseley (1977) and crystals of this material gave the same diffraction effects that had been previously observed. All electron diffraction patterns were obtained using a JEOL 100CX electron microscope with a ±60° double-tilt goniometer stage, and an accelerating voltage of 100kV.

Some preliminary experimentation on the optical bench suggested that diffraction patterns similar to those observed could be produced by moiré effects resulting from the overlapping of two or more crystallites. After some further experimentation it was found that good agreement with the observed patterns was obtained by using optical diffraction masks consisting of a simple square grid of circular apertures and in Figs. 1(d) and (e) we show optical diffraction patterns that were obtained corresponding to the electron diffraction examples of Figs. 1(a) and 4(b). The masks, which consisted of 50 μm circular apertures on a 100 μm grid, were made using the method of Harburn, Miller & Welberry (1974) and the diffraction patterns obtained using an optical diffractometer as described by Harburn, Taylor & Welberry (1975).

To obtain these (and other) examples it was necessary only to adjust the mutual orientation of the overlapping diffraction masks until the required pattern was observed. For the example of Figs. 1(d) and (e) the mutual orientations were ~45 and 26.6° respectively. In each case one mask was placed in a position to partly cover the other mask. This ensured that the main diffraction peaks were still clearly recognizable in the resulting pattern. Observed electron diffraction patterns evidently had varying degrees of overlap as some had clearly discernible main diffraction peaks, and others not.

The more complex electron diffraction pattern shown in Fig. 1(c) is clearly the convolution of three differently oriented lattice transforms. We were unable to match the particular angles required to simulate this in an optical experiment, for two reasons. The first was because one angle of misalignment was very small and the consequent spacing of the moiré fringes large. Because of phase errors introduced by variations of film thickness in our optical masks the coherence of our laser light is lost over distances of this magnitude, and resolution of the resulting fine-scale diffraction peaks is destroyed. The second reason was the necessity to use a reasonably large aperture size (relative to the lattice repeat) in order to have a measurable total
transmission through three such diffraction masks. The smaller the aperture used, the more orders of subsidiary maxima will be visible around each main diffraction peak. This is only of importance for the very small misalignment angles when all such peaks are clearly identifiable as originating from the same main diffraction beam. Despite these limitations, the similarity of the observed electron diffraction pattern with the optical simulation shown in Fig. 1(f) is apparent. The rotational misalignments were calculated to be 1.7° and 9.7° for the electron diffraction pattern while for the optical pattern we used rotations of 3.5° and 18°.

From these optical experiments it was clear that the electron diffraction patterns were caused by superimposed thin flakes of a material with a layer structure and relatively weak inter-layer bonding, and whose structure was well approximated by a simple square grid of circular apertures. This information was instrumental in our being able to identify the material as LaOI.

LaOI has the PbFCl (matlockite) structure (Sillen & Nylander, 1941; Wyckoff, 1965), space group $P4/nmm$, with cell parameters $a = 4.144$, $c = 9.126\text{Å}$. The structure consists essentially of two-dimensional sheets of edge-sharing $\text{OLa}_4$ tetrahedra separated by a double layer of iodine atoms. The bonding between the two iodine layers is very weak and hence provides a ready explanation for the tendency for rotational misalignment. Viewed in projection down [001] the La and I atoms from adjacent layers are superimposed and form a simple square mesh with the O’s positioned at the centre of the squares (see Fig. 2). The structure in the [001] projection is thus well represented in the optical diffraction experiment by a simple square grid of circular apertures, the scattering of the

![Fig. 2. [001] projection of the structure of LaOI. The two half-layers, [OLa₄] tetrahedra and [ILa₄] square pyramids, are drawn separately; large circles represent I and La superimposed and small circles represent O; I at $+0.34c$, La at $+0.13c$ and O at $0.0c$.](image)

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Fig. 1. Comparison of electron diffraction photographs, (a), (b), (c), of LaOI viewed down [001], with optical diffraction photographs, (d), (e), (f), of rotation moiré patterns made by overlapping masks of a simple square array of circular apertures. See text for details.
oxygen being negligible in comparison to that from the lanthanums and iodines.

Electron diffraction patterns were observed with many different degrees of rotational misalignment. Ones in which the angle of rotation was small (< 10°) were particularly numerous. For patterns with much higher misalignments, however, it became apparent that these occurred at angles close to (but not exactly at) special values such as \( \tan^{-1}(1) \) and \( \tan^{-1}(1/2) \), as typified by those in Figs. 1(a) and (b), and also \( \tan^{-1}(2/3) \). We must conclude from this that the rotated sheets of LaOI are still in sufficiently intimate contact that the interlayer \([-\text{La--I--}]\) bond strength is comparable with that in the undeformed crystal. Preferred (minimum potential) sites are thus assumed by the two opposing layers of iodines – indeed at other than very small angles of rotation these low-energy positions are far more probable. The observed diffraction effects indicate the existence of a fairly wide range of 'semi-commensurate' superstructures of LaOI based on this principle. Further work on the system is in progress.

References


