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Application of the Grain-counting Technique to Electron Diffraction Experiments

B. TURMAN and PER ANDERSEN

Department of Chemistry, University of Oslo, Oslo 3, Norway

The grain-counting technique has been applied to determine the scattered electron intensity recorded on photographic plates from gas electron diffraction experiments. Photographic plates were made with 1 μ emulsion thickness from an Ilford K-5 nuclear research emulsion. A microscope focused the grain image into a television camera and signals from the camera were analyzed by a special logic circuit.

The scattering pictures from CCl_4 and CO_2 were studied using this technique and the results compared with calculated theoretical curves based on the well known structures of these molecules.

In the normal electron diffraction experiment a photographic plate is used to record scattered electron intensity. The photographic density of the exposed plate is measured with a photometer and converted to electron exposure. A new technique was developed at Uppsala University for obtaining intensity information from plates.[1-3] In this method, the number of developed grains per unit area in the emulsion is observed and related to exposure. Rundgren pointed out that this method would be useful for intensity measurements in the electron diffraction experiment.[4] Use of the grain-counting method in electron diffraction work has been studied in this laboratory, and the results are reported in this paper.

EXPERIMENTAL ARRANGEMENT

The principle of operation of the grain counting equipment is described in Ref. 2. A 100-power microscope focused the grain image into a television camera, the observation area on the plate being 0.01 mm^2. Signals from the camera were detected and analyzed by a special logic circuit and data output was printed on paper tape. Dark field illumination, with a tungsten lamp source, was used in the microscope. With dark-field illumination, light was projected downward onto the silver grains, so that grains were viewed as bright objects against a dark background. The image contrast was higher than that observed with bright-field illumination, and dust particles on the optical components would not be mistaken for grains. Since oil immersion was required on both sides of the glass plate, the use of dark-field illumination presented a special problem. The light intensity was found to be dependent on the oil film thickness, so that care was required to maintain this film at a constant thickness during a scan across the plate. The rectangular stage movement provided on the microscope was used to scan through the diffraction pattern. The radial distance from the pattern center was determined by a dial indicator to an accuracy of 0.01 mm. The microscope and television camera were mounted on an isolated table to protect them from mechanical vibration.

The depth-of-focus of the microscope objective lens was quite small, of the order of 1 μ. The thinnest emulsion available commercially was about 5 μ, so that a subjective error could be made in focusing the microscope. To eliminate this problem, plates with 1 μ emulsion thickness were made in this laboratory. Ilford K-5 nuclear research emulsion in gel form was used. After the emulsion was melted at 50°C, it was poured over a treated glass plate. A stainless steel blade was pulled across the plate, spreading the emulsion uniformly and setting the desired emulsion thickness. The emulsion was then allowed to cool slowly.

The electronic equipment was manufactured by Securitas Corporation of Sweden. The television camera and power supply were of standard design. The output signal from the camera was led into a detector-discriminator circuit. The discriminator level was adjusted so that noise was eliminated and only pulses

arising from the grain image were analyzed in the logic circuit. The logic circuit could be operated in one of three modes, called "project", "count", and "area". In the first mode, all pulses coming from a grain image were counted. Since the grain image dimensions in our apparatus were typically about 7 times as large as the television scan width, approximately 7 pulses were produced from one grain. In effect, the number of pulses in this mode gave the length of the grain projection on an axis perpendicular to the television scan direction. In the second mode, only one pulse was produced per grain. To accomplish this feat, a delay line and anti-coincidence circuit were provided. The pulse from a grain image was divided into two parts: one part went directly to the anti-coincidence circuit, while the second pulse traveled through the delay line. The time delay was adjusted so that this delayed signal arrived at the anti-coincidence circuit simultaneously with the next direct pulse. The direct pulse was blocked under these conditions. Thus only the first direct pulse was passed, and the counting unit counted total number of grains. In the area mode, both the total number of pulses and the time duration of each pulse were measured, so that the output from the counter was related to the area of the grains. A series of reproducibility measurements were made with the count and project modes. The project mode was better in this respect than the count mode; approximately 1 % deviation in the project data and 5 % deviation in the count data were observed. Averaging 10 measurements with the count mode improved the reproducibility to a figure similar to that of the project mode.

Irregularities in grain shape could upset the operation of the grain counting system. For instance, a crescent-shaped grain was often counted twice in the count mode, while a long, narrow grain could give a misleading projection value in the project mode. The error due to this effect, however, was small. One solution to this problem might be the use of physical development [6] for the plates, since grain shape and size could be regulated in this process.

DATA ANALYSIS AND RESULTS

Two molecules were studied in this experiment: CCl_4 and CO_2. The molecular structures and vibrational data of these two compounds are of course well documented, so that theoretical scattering functions can be assumed to represent ideal experimental results. The data for CCl_4 were taken with the count mode, while the project mode was used for CO_2 data. Each plate was scanned at least three times. At each measurement point along the scan line the number of grains within at least three different areas was averaged. The three scans were then averaged together with the statistical averaging program of Stølevik.[5] A total number of about 1000 counts was taken at each measurement point. Next, the sector correction was applied and the theoretical background removed. Finally, a smooth background function through the experimental points was determined by a least squares program written by Strand.[5] Only the molecular scattering function remained after subtraction of the background function.

It was found that the measured intensity required a blackness correction. The one-hit blackness correction,[6] responsible for the exposure characteristics of emulsions at higher densities, showed practically no effect at the low photographic density used in this experiment. The main effect appeared to be due to the formation of grain clusters which were counted as single grains. Since all of the grains were observed to lie essentially in a plane, a two-dimensional theory should be sufficient to describe the clustering. Considering only two and three-grain clusters, the corrected intensity would have the form $(1+\alpha N)(1+\beta N)N$, where N was the number of grains counted. A least squares procedure was used to find the values of α and β which gave the best agreement between corrected experimental molecular intensity and theoretical molecular intensity. These parameters were: $\alpha = 0.04$, $\beta = 0.0018$. A calculation of the effect of four-grain clustering showed less than 1 % change in the correction. Reasonable agreement with these values for the parameters was obtained from a theoretical calculation based on the observed grain

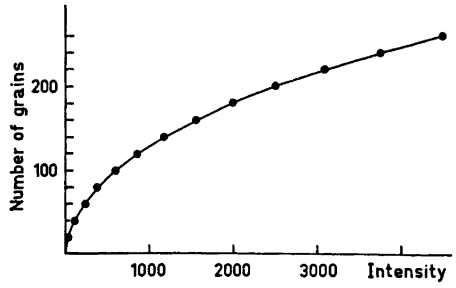

Fig. 1. Corrected intensity of the form $(1+0.04N)(1+0.0018N)N$ where N is the number of grains counted.

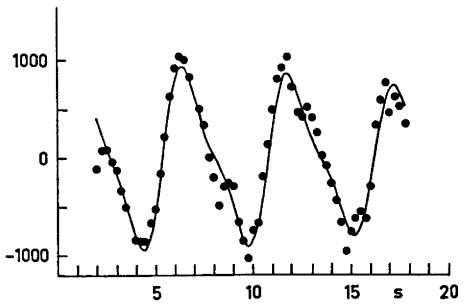

Fig. 2. Theoretical intensity curve for CO_2(—) and corresponding experimental points (●) from the grain-counting experiment.

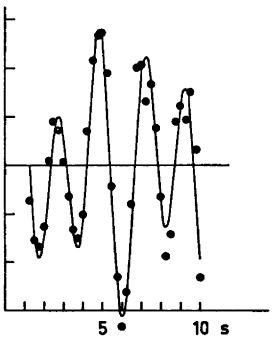

Fig. 3. Theoretical intensity curve for CCl_4(—) and the corresponding experimental points (●) from the grain-counting experiment.

size. Fig. 1 shows the form of this correction curve.

The project mode data were divided by the mean projection per grain to obtain the number of grains counted. This ratio was determined by counting with both the project and count modes at a large number of points on the photographic plate, and then treating the data with the least squares method. The value of the ratio was 7.43. This number is of course dependent on the magnification of the microscope and the grain size of the emulsion.

Experimental results from CO_2 and CCl_4 scattering patterns are compared with theoretical curves in Figs. 2 and 3. As stated earlier, these molecules have been so thoroughly studied that any discrepancies between theory and experiment here must be interpreted as experimental errors. There are several bad points which deviate considerably from the theoretical curve for CO_2. The least squares calculation of blackness correction will be influenced by these points, since the criterion is to minimize the sum of the squared deviations. Therefore the calculated blackness correction may be a bit conservative, so that the experimental data at low s-value may agree with theory slightly better than shown here. The CCl_4 data have been multiplied by the blackness correction determined from the CO_2 curves. Again there is considerable deviation from the theoretical curve, and a small increase in blackness correction for small s-values would be helpful. Random deviations in the number of grains developed per unit area in the emulsion are probably the major source of error in these measurements. Since a total of about 1000 grains were counted at each s-value, the statistical error is approximately 3 % on the total scattering intensity, or roughly 20 % on the molecular scattering. This error can be reduced by collecting a larger number of counts. For example, the plate could be scanned in concentric circles, thereby assuring a very large number of counts. Another advantage in the circular scan would be that any emulsion imperfections could be easily detected and discarded. The collection of large numbers of counts demands the use of an automated system, but the problem of automatically focusing the microscope has yet to be solved.

The main advantage in using the grain counting technique rather than the photometer is that a much smaller electron exposure is required when the individual grains are counted. In the present experiment, only one-tenth the normal exposure was used. The maximum number of grains counted was around 200 grains per 0.01 mm², and from Fig. 1 it appears that an even lower exposure would be better. This lower exposure could be of great benefit when analyzing highly reactive compounds, or small quantities of a compound. In addition, the grain-counting method should be useful in those problems in X-ray crystallography where a reduction of exposure time is important.

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