

X-ray Study of Diffuse Streak Diffraction Pattern from Silicon Single Crystals

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Diffuse X-ray scattering by silicon single crystals has been detected on the film by the use of a doubly bent crystal monochromator. The intensities of one diffuse streak were measured at 83°K and 273°K with a scintillation counter spectrometer. With rising temperature the intensity of the diffuse streaks was increased, confirming their thermal origin. In order to examine the scattering in detail, measurements of the absolute thermal scattering power were made through a large region of the (101) reciprocal lattice plane at 293°K. These measurements were compared with the theoretical values of the thermal scattering power, given by the theory developed by Laval, in which temperature vibrations are expressed in terms of elastic waves. The first-order term only was calculated and higher-order terms were neglected. The measurements are in semi-quantitative agreement with this theory.

Introduction

A characteristic streak X-ray diffraction pattern from silicon single crystals was first noticed by Kodera, Kitamura & Honjo (1963) in a photograph taken with filtered Mo radiation parallel to the [100] axis. This characteristic type of diffuse scattering has also been seen in electron diffraction diagrams, as well as in X-ray diagrams on some other substances. Honjo, Kodera & Kitamura (1964) inferred that the streak patterns by silicon single crystals indicate a predominant clustered motion of linear scatterers along $\langle 110 \rangle$ directions, the scatterers consisting of zigzag chains of the nearest neighbour silicon atoms. Komatsu (1964) gave a revised interpretation in terms of the dynamical theory of lattice vibrations. He considered transverse acoustic waves, polarized in the direction of the atomic chains, having predominantly low frequencies. This gives a particular intensity distribution restricted to the $\{110\}$ reciprocal planes, but without diffuse scattering in the reciprocal planes passing through the origin. A quantitative analysis of the intensity distribution of diffuse streaks in silicon single crystals has not yet been given.

Recent X-ray studies of diffuse thermal scattering on silicon single crystals were made by Corbeau (1964) and Banerjee (1967). Their measurements were confined to several special directions in the crystal lattice in order to obtain the dispersion relations of lattice vibrations (Corbeau) or to determine the Compton scattering of silicon crystal (Banerjee, 1967). Dispersion curves in special directions on crystals which have a diamond structure were measured also by Brockhouse & Iyengar (1958) and by Dolling (1962) by means of inelastic neutron scattering. In all these studies no special attention has been given to the streak diffusion pattern in silicon single crystals. The explanation of the origin of the streaks seems to require more systematic experimental and theoretical studies. Thus we decided to

make our measurements of scattered X-ray radiation throughout a large region of reciprocal space paying special attention to the (101) plane.

Experimental

(a) Recording of diffuse streaks and measurements of their variation with temperature

The silicon single crystal used for the experiment and prepared by careful grinding, polishing and etching was approximately $5 \times 5 \times 0.1$ mm³ and cut so that its face was parallel to the (111) planes. X-rays from a well stabilized, full wave rectified copper target tube run at 40 kV and 16 mA were monochromatized by a toroidally bent LiF crystal plate, set to reflect the Cu $K\alpha$ radiation on the (200) planes. The beam was focused on the face of the crystal which was oriented with the axis [111] parallel to the beam. The transmission photographs were obtained both on a plane film and on a cylindrical film [Fig. 1(a), (b)]. Besides Laue spots conspicuous diffuse streaks can be seen in both photographs. Fig. 1(c) represents the projection, on the cylinder, of the intersections of the $\{110\}$ reciprocal planes with the Ewald sphere, which corresponds to the setting of the crystal. The diffuse streaks in Fig. 1(b) correspond to the parts of curves indicated by thicker lines in Fig. 1(c). Thus it is evident that the diffuse streaks correspond to the intersections of the $\{110\}$ reciprocal planes with the Ewald sphere.

In order to verify their thermal origin the intensities of one of these streaks, situated in Fig. 1(b) between the 111 and 313 reflexions, were measured at 273°K and 83°K by means of a recording scintillation counter spectrometer. The crystal, placed in an evacuated chamber, was mounted on a goniometer head which was in thermal contact with liquid nitrogen. The temperature of the crystal was measured with a thermocouple fastened to the support of the crystal.

The intensities obtained are represented in Fig. 2. The full curve and the dashed curve represent the results of the measurements at 83°K and 293°K respec-

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tively. An eight-second counting interval only was used to avoid the formation of ice on the silicon surface during the measurements. Thus the deviations of the measured points from the smoothed curves are considerable.

(b) *Measurements of the absolute magnitude of the thermal scattering*

The measurements of the absolute magnitude of the thermal diffuse scattering were made at room temperature. X-ray data and the method of monochromatization were the same as in (a). The crystal used was a single crystal with dimensions $15 \times 15 \times 4$ mm³ cut so that its face was parallel to the (111) planes. After polishing and etching, the crystal was placed in an evacuated chamber. The reflected intensities were detected with a scintillation counter (NaI crystal activated with Tl). The measurements of the diffuse reflexions were carried out by placing the crystal and the detector in such a position that the measurements could be done in the direction [111] of the reciprocal lattice from $2 \sin \theta / \lambda = 0.358.10^8$ to $0.917.10^8$, as well as in 19 additional directions, in the $(\bar{1}01)$ reciprocal plane, which varied in steps of two degrees on both sides of the [111] direction, as visible from Table 1 and Fig. 3. The intensity of the direct beam was evaluated at the beginning and at the end of the measurements of the intensities of scattered radiation corresponding to a given direction. A three-minute counting interval was used in the measurements of the scattered radiation and ten three-minute measurements were made for each evaluation of the direct beam. This made it possible to explore the part of the $(\bar{1}01)$ reciprocal plane lying between 111, 131, 313 and 333 reciprocal lattice points (relps). The setting and the recording were

made automatically. The readings obtained from the scaler were automatically recorded by means of a print-out unit which converted the readings of the scaler into numbers. The harmonics of the characteristic radiation could not be completely eliminated with the discriminator only. Therefore an aluminum filter was used to estimate the intensities of the half-wavelength reflected by the monochromator. The fluctuation of the scattered radiation flux printed out was less than 3%. This flux, $i(\mathbf{X})$, is related to the diffuse scattering power $\mathcal{I}(\mathbf{X})$ in the relation given by Guinier (1964). $\mathcal{I}(\mathbf{X})$, modified to express the scattering relating to an electron of the crystal, may be written as follows:

$$\mathcal{I}(\mathbf{X}) = \frac{i(\mathbf{X})\mu \cdot \varrho(1 + \sin \alpha / \sin \beta)v_1(1 + \cos^2 2\alpha')}{7.90 \cdot 10^{-26}\varepsilon E_0(1 + \cos^2 2\alpha' \cos^2 2\theta)d\omega} \quad (1)$$

where the symbols have the following meanings:

- \mathbf{X} vector of diffuse scattering. $|\mathbf{X}| = 2 \sin \theta / \lambda$;
- μ mass absorption coefficient of the sample ($60.6 \text{ cm}^2\text{g}^{-1}$);
- ϱ density of the sample (2.4 g.cm^{-3});
- α and β angles of incidence and of diffuse reflexion of X-rays on the silicon crystal;
- α' angle of reflexion on the monochromator;
- v_1 volume of the unit cell ($160.19 \cdot 10^{-24} \text{ cm}^3$);
- ε number of electrons in a unit cell;
- E_0 total flux of the incident X-ray beam;
- $d\omega$ solid angle of X-rays entering the counter (1.07×10^{-3} sterad);
- 2θ angle of diffuse scattering.

The ratio $i(\mathbf{X})/E_0$, in (1), was obtained experimentally by dividing the measured flux of the diffusely reflected radiation by that of the incident radiation. It was obtained as the ratio between the number of counts,

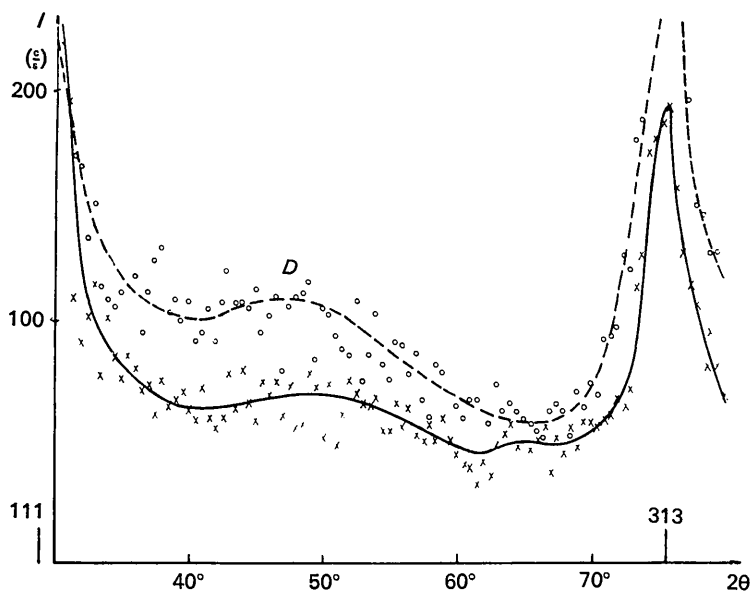


Fig. 2. Measured relative intensities between (111) and (313) relps, at 83°K (full curve) and 293°K (dashed curve). The maximum marked with *D* belongs to the diffuse streak.

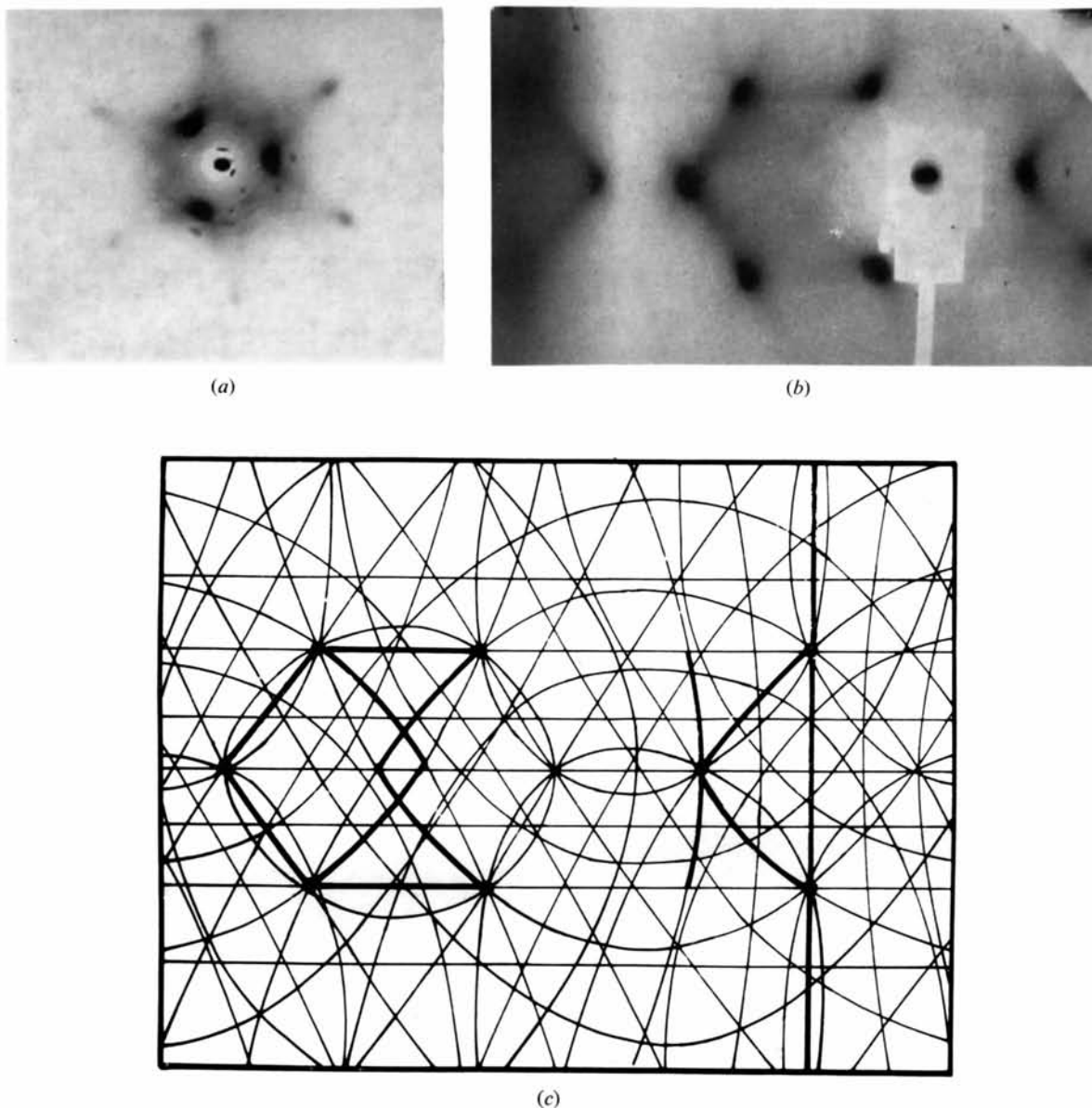


Fig. 1. (a) Stationary crystal X-ray transmission photograph on a plane film. The photograph is taken with Cu radiation monochromatized by a toroidally bent LiF crystal plate, set to reflect the Cu $K\alpha$ radiation on the (200) planes. The silicon single crystal was oriented with the [111] axis parallel to the beam. Exposure time: 5 hours. (b) Same as (a) but photographed on a cylindrical film. $[\bar{1}01]$ axis parallel to the cylinder axis. (c) The curves represent the projection on the cylinder of the intersections of the {110} reciprocal planes with the Ewald sphere. $\langle 111 \rangle$ axis parallel to the beam, $\langle 110 \rangle$ parallel to the chamber axis.

recorded in unit time, when the diffuse radiation is entering the detector, and the number of counts in unit time when the whole of the direct beam is allowed to enter the detector. This ratio being small (about 10^{-7}), it was necessary to reduce the flux of the direct beam by carefully calibrated nickel foils.

The measurements being made far enough from the relps, divergence corrections could be neglected. From the diffuse scattering power calculated by (1), the Compton modified component, given by Freeman (1959), was subtracted and the remainder treated as the thermal diffuse scattering $I(X)$. The results are given in Table 1 and shown in Fig. 4(a) in the form of a contour plot of equidiffusion lines.

Calculation of the first-order thermal diffuse scattering power

Following Laval (1954) the first-order thermal scattering power P , relating to the scattering of an electron of the crystal, is given by

$$P = \frac{|X|^2}{em} \sum_{\gamma=1}^6 \left(\frac{W}{v^2} \right)_{S_\gamma} |\Phi_{S_\gamma}|^2.$$

The new symbols have the following meanings:

m mass of the unit cell;

$$\left(\frac{W}{v^2} \right)_{S_\gamma} = \frac{h}{v_{S_\gamma}} \left[\frac{1}{\left(\exp \frac{h v_{S_\gamma}}{kT} \right) - 1} + \frac{1}{2} \right];$$

- h Planck's constant;
- k Boltzmann's constant;
- T temperature;
- v_{S_γ} frequency of the oscillation S_γ , S being the wave vector;

$$\Phi_{S_\gamma} = \sum_j f_j' \chi_{S_\gamma}^j \exp [i2\pi(\mathbf{M}\mathbf{j} + \phi_{S_\gamma}^j)];$$

- f_j' atomic structure factor f_j , multiplied by the Debye-Waller factor H_j ;
- \mathbf{M} vector of the lattice translation;
- \mathbf{j} average position of the j th atom in the unit cell;

$$X_{S_\gamma}^j = \frac{1}{|X|} \left(\frac{m}{m_j} \right)^{1/2} \left| \sum_\alpha X_\alpha q_{\alpha S_\gamma}^j \exp (i2\pi\phi_{\alpha S_\gamma}^j) \right|; (\alpha = 1, 2, 3)$$

- m_j mass of the j th atom;
- $q_{\alpha S_\gamma}^j$ represents modulus and $2\pi\phi_{\alpha S_\gamma}^j$ phase of $\zeta_{\alpha S_\gamma}^j$, defined by

$$\zeta_{\alpha S_\gamma}^j = q_{\alpha S_\gamma}^j \exp [-i2\pi(\mathbf{S}\mathbf{j} - \phi_{\alpha S_\gamma}^j)].$$

$q_{\alpha S_\gamma}^j$ are the components of the proper vectors of the dynamical matrix (Fourier matrix). For the diamond lattice type, to which the silicon lattice belongs, the form of the matrix was determined by Smith (1948). Generally, the form of this matrix is as follows:

$$\begin{bmatrix} F & J & K & A & B & C \\ J & G & L & B & A & E \\ K & L & H & C & E & A \\ A^* & B^* & C^* & F & J & K \\ B^* & A^* & E^* & J & G & L \\ C^* & E^* & A^* & K & L & H \end{bmatrix} \quad (3)$$

The approximation to the frequency distribution is obtained by considering the second-neighbour force as central. Then:

$$F = 4\{\alpha + \mu\{2 - \cos(\pi S_x) \cos(\pi S_y) - \cos(\pi S_z) \cos(\pi S_x)\}\}$$

$$J = 4\mu \sin(\pi S_x) \sin(\pi S_y)$$

$$K = 4\mu \sin(\pi S_z) \sin(\pi S_x)$$

$$L = 4\mu \sin(\pi S_y) \sin(\pi S_z)$$

$$G = 4\{\alpha + \mu\{2 - \cos(\pi S_y) \cos(\pi S_z) - \cos(\pi S_x) \cos(\pi S_y)\}\}$$

$$A = -\alpha[1 + \exp\{-\pi i(S_x + S_y)\} + \exp\{-\pi i(S_z + S_x)\} + \exp\{-\pi i(S_y + S_z)\}]$$

$$B = -\beta[1 + \exp\{-\pi i(S_x + S_y)\} - \exp\{-\pi i(S_z + S_x)\} - \exp\{-\pi i(S_y + S_z)\}]$$

$$C = -\beta[1 - \exp\{-\pi i(S_x + S_y)\} + \exp\{-\pi i(S_z + S_x)\} - \exp\{-\pi i(S_y + S_z)\}]$$

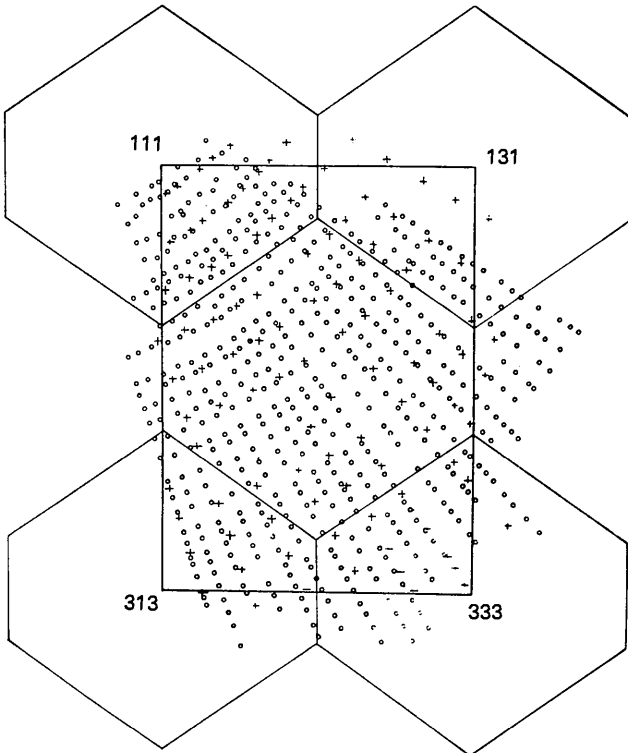


Fig. 3. The $(\bar{1}01)$ plane of a reciprocal lattice of silicon, each lattice surrounded by its own zone. Small circles indicate the points of measurements of scattered intensities, and crosses the points in which the first-order thermal scattering power was calculated.

(marked with D) diminishes as the temperature falls from 293°K to 83°K. Thus the temperature dependence of the intensity of the diffuse streak proves the thermal origin of the streak. At the same time spot 111 becomes stronger and spot 313 weaker. It is possible that the thermal expansion of the crystal moved relp 111 nearer to the Ewald sphere and 313 further from it, thus causing the observed changes in intensity.

Fig.4(a) represents a contour plot of the measured power of thermal diffuse scattering at 293°K, which was obtained by subtracting the Compton modified scattering, calculated by Freeman (1959), from the measured diffuse scattering. The occurrence of a comparatively strong 'forbidden' maximum in relp 222 is explained by Renninger (1937) and Heidenreich (1950) on the basis of the dynamical theory and is to be expected in diamond structures. This maximum influences the aspect of the equidiffusion contours obtained by measurements, but does not exist in the calculated contour plot represented in Fig.4(b). Experimentally a quantitatively stronger diffusion streak was found than by calculation. A better fit would probably

be attained with a more rigorous calculation of the vibration frequencies, without the approximation of the frequency distribution. Uncertainties exist also in the determination of the Compton modified scattering. In some recent articles on the Compton effect, Banerjee (1964, 1967) describes anomalies in the values of the intensities of scattered radiation. However, in both Fig.4(a) and Fig.4(b) the diffuse streak between 313 and 333 relps is evident. Moreover, the calculated streaks are about equally widespread as those experimentally observed. Thus we may conclude that thermal diffuse scattering is concentrated in the {110} reciprocal lattice planes, the greatest intensity appearing between relps, and that the diffuse streak diffraction patterns from silicon single crystals may be explained in terms of thermal scattering.

It is interesting to make a comparison between the diffuse scattering pattern of silicon and those observed in diamonds and barium titanate. In the case of diamonds the extra X-ray reflexions are two of kinds. One, dependent upon temperature and identified with thermal diffuse scattering, and another largely independent

Table 2. Calculated values of the first-order thermal diffuse scattering power P

Direction	$x = \frac{2 \sin \theta}{\lambda} \cdot 10^{-8}$	P	Direction	$x = \frac{2 \sin \theta}{\lambda} \cdot 10^{-8}$	P	
[2 5 2]	0.454	0.211	[1 1 1]	0.358	0.521	
	0.517	0.356		0.401	0.286	
	0.558	0.398		0.454	0.221	
	0.599	1.341		0.517	0.141	
	0.629	0.168		0.558	0.118	
[1 2 1]	0.401	0.183		0.599	0.085	
	0.454	0.226		0.668	0.101	
	0.517	0.204		0.706	0.157	
	0.558	0.156		0.744	0.209	
	0.599	0.090		0.834	0.354	
[3 5 3]	0.629	0.050		0.876	0.516	
	0.401	0.194		0.917	1.091	
	0.454	0.227		[7 6 7]	0.358	0.374
	0.517	0.192			0.401	0.307
	0.558	0.136			0.454	0.220
0.599	0.065	0.517	0.193			
0.697	0.116	0.558	0.190			
[2 3 2]	0.744	0.144	0.599		0.122	
	0.358	0.173	0.668		0.017	
	0.401	0.244	0.696		0.171	
	0.454	0.229	0.744		0.496	
	0.517	0.211	0.799		0.301	
[3 4 3]	0.558	0.115	0.834		0.427	
	0.599	0.021	0.876		0.598	
	0.697	0.061	0.917		0.848	
	0.744	0.189	[4 3 4]		0.358	0.269
	0.358	0.338			0.401	0.313
0.401	0.272	0.454		0.234		
0.454	0.216	0.517		0.164		
0.517	0.211	0.558		0.156		
[5 6 5]	0.558	0.157		0.599	0.091	
	0.599	0.070		0.629	0.029	
	0.668	0.087		0.697	0.073	
	0.697	0.106		0.744	0.231	
	0.744	0.187		0.790	0.345	
[5 6 5]	0.799	0.336		0.834	0.376	
	0.358	0.493		0.876	0.464	
	0.401	0.282		[5 3 5]	0.401	0.242
	0.454	0.271			0.454	0.251
	0.517	0.154			0.517	0.214
0.558	0.067	0.558	0.120			
0.599	0.032	0.599	0.071			
[5 6 5]	0.668	0.133	0.699		0.049	
	0.697	0.205	0.744		0.193	
	0.744	0.205	0.799		0.361	
	0.799	0.311	0.834		0.480	
	0.834	0.468	[2 1 2]		0.517	0.247
0.876	0.473	0.558			0.179	
0.629	0.014	0.599			0.066	
0.668	0.015	0.697			0.035	
0.697	0.029	0.744			0.262	
[5 2 5]	0.744	1.248	0.790		0.564	
	0.799		0.834	0.721		

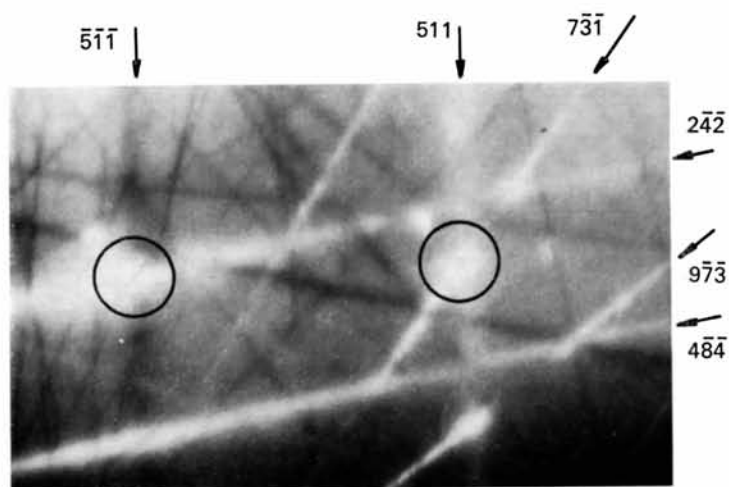


Fig.1. Transmission Kikuchi pattern from natural spinel, $MgAl_2O_4$, showing split lines (encircled), enhanced and diminished line segments. Nominal voltage in all Figures: 100 kV.

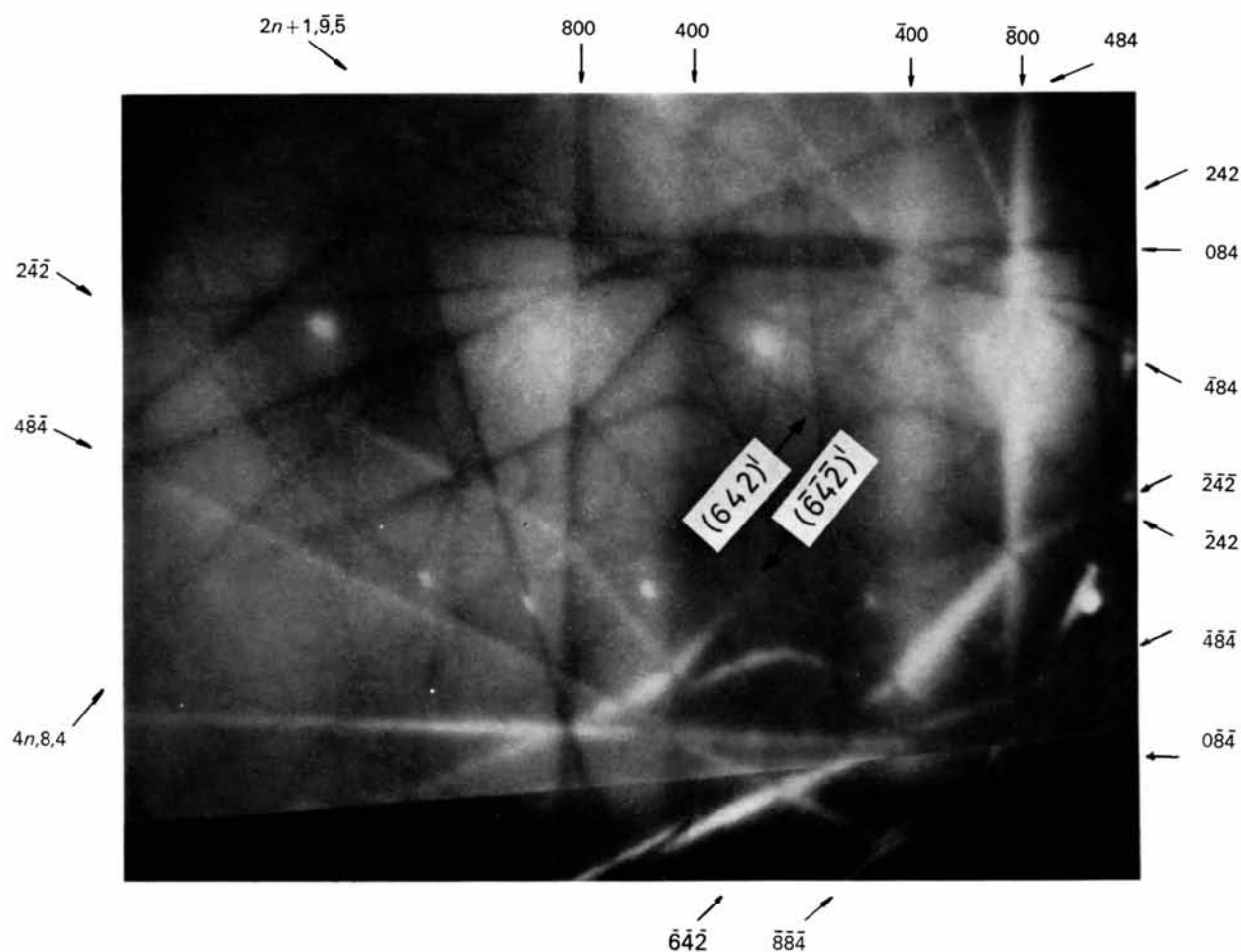


Fig.2. Transmission Kikuchi pattern showing split lines, enhanced and diminished line segments, displaced lines, e.g. $\pm 642'$.

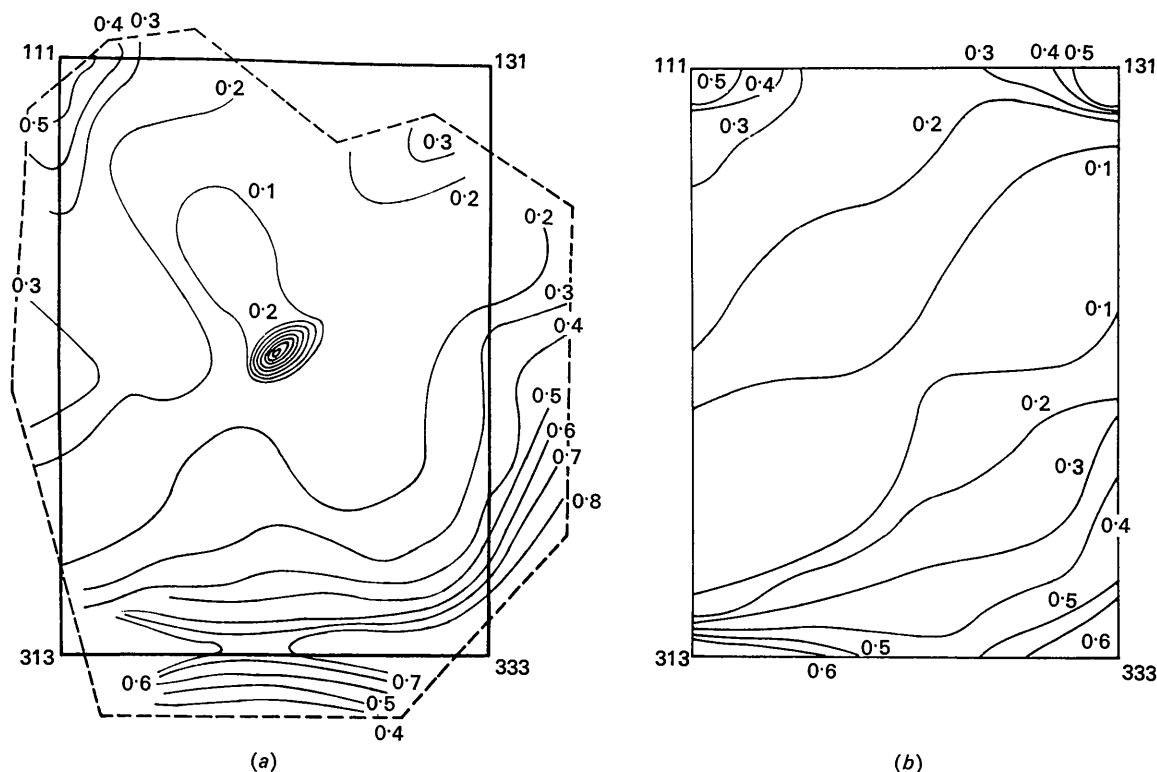


Fig. 4. Equi-intensity contour in the $(\bar{1}01)$ plane: (a) from measured intensities. Around relp (222) each succeeding contour line represents diffuse intensity higher by 0.1 than the preceding line. (b) from calculated first-order thermal scattering power.

of temperature, for which Hoerni & Wooster (1955) established the form of spikes in reciprocal space. The X-ray diffraction spikes of diamond have been attributed to defects and are entirely absent in some diamonds. Diffuse scattering of X-rays and electrons from BaTiO_3 single crystals was attributed by Harada, Watanabe, Kodera & Honjo (1965) to thermal diffuse scattering due to low-frequency transverse optic lattice waves, but Comes, Lambert & Guinier (1968) attributed it to a partially disordered structure.

In our measurements on silicon single crystals we did not find any scattering corresponding to spikes in diamonds. Compared with streaks given by BaTiO_3 , diffuse streaks in silicon are wider, and wide streaks are characteristic for diffuse scattering of a really thermal origin.

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