Scattering of Electrons by Stibnite and Galena

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A study has been made of the scattering of 20–60 kv electrons, produced in a hot cathode tube, by cleavage surfaces of stibnite and galena. The patterns from stibnite consist of spots, Kikuchi lines, bands, circles and parabolas. The spots are a surface grating effect with high resolving power for both surface directions. It is concluded that the crystal has relatively large mosaic units and that collisions with atoms, involving small energy losses, cause high absorption of the primary beam as it penetrates the crystal. Inelastic collisions, producing excitation of the thermal vibrations of the crystal, are considered. They cause increased scattering at angles just larger than the Bragg reflection angles and thus give a reason for the bands. The circles are considered to arise from the localizing of an electron's wave packet to the neighborhood of a single row of atoms, a process initiated by an inelastic encounter with a single atom. The measurements indicate a potential difference of about 26 volts between the row of atoms and the outside of the crystal. The parabolas, which occur also with galena, are thought to be due to the confinement of an electron to a single plane of atoms.

INTRODUCTION

As first shown by Kikuchi and Nishikawa[1] for calcite, the diffraction of high energy electrons by crystal cleavage surfaces consists of a pattern of intersecting straight lines and bands and a number of spots. Kikuchi[2] has explained the lines as due to Bragg reflections of the diffusely scattered electrons in the crystal. The breadth of the Kikuchi lines has been worked out by Shinohara,[3] using Bethe's theory of electrons in crystals. It is sometimes sufficient to fill the space between a pair of parallel Kikuchi lines, thus affording an explanation of the bands.

The present paper is concerned chiefly with the scattering by stibnite crystals in which some new effects are observed.

APPARATUS

The apparatus is practically the same as that described by G. P. Thomson and C. G. Fraser,[4] except that a hot filament source of electrons replaces the gas discharge tube and the high tension is produced by a transformer in conjunction with rectifying Kenotrons and smoothing condensers. The cathode consists of a cylindrical nickel box with a 0.5 mm hole at one end and a filament of Konel strip just behind the hole. The electrons emerging from the hole, under the influence of the accelerating field, come to a focus just outside the hole. It is thus only necessary to have a single pinhole at the entrance to the crystal chamber in order to obtain a sharply defined beam. A ground-in plug, to which was attached a strip of metal carrying several pinholes of diameters varying down to 0.05 mm, allowed beams of any desired cross section to be obtained. The crystal could then be set by visual observation at the fluorescent screen with a large pinhole, and a fine pinhole substituted in making the photograph.

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[1] Kikuchi and Nishikawa, Proc. Imp. Acad. Japan **4**, 475 (1928).

[2] S. Kikuchi, Jap. J. Phys. **5**, 83 (1928–29).

[3] Shinohara, Inst. Phys. Chem. Res. (Tokyo) **18**, 221 (1932).

[4] Thomson and Fraser, Proc. Roy. Soc. **A128**, 641 (1930).

EXPERIMENTS WITH STIBNITE

Stibnite Sb_2S_3 is orthorhombic with a, b, $c=11.39$, 11.48, 3.89[5] and cleaves perpendicular to the b axis. Fig. 1 is a photograph taken with the a axis in the plane of incidence, which is horizontal. The pattern consists of spots, lines, bands, circles and parabolas.

The spots

The spots appear to be a surface grating effect. The reflection conditions for this are

$$\cos\alpha = \cos\alpha_0 - h\lambda/a$$

$$\cos\gamma = \cos\gamma_0 - l\lambda/c$$

[5] Gottfried, Zeits. f. Krist. **65**, 428 (1927).

where α_0, γ_0; α, γ are the angles the incident and reflected beams make with the a and c axes.

Let L be the distance from crystal to plate and take all angles to be small. Then the first condition gives a series of concentric circles of radii given by

$$r_h^2 = r_0^2 + 2L^2 h\lambda/a,$$

while the second condition gives a set of parallel layer lines separated by an interval $\eta = L\lambda/c$. From these we obtain $c/a = (r_{h+1}^2 - r_h^2)/2L\eta$. Table I shows that $(r_{h+1}^2 - r_h^2)/\eta$ is independent of h and also of the voltage. The mean value of c/a is found to be 0.339 agreeing with Gottfried's x-ray value of 0.342. The mean value of c obtained from $\eta = L\lambda/c$ is 3.86A agreeing with the x-ray value of 3.89A.

Kirchner and Raether[6] have found that at small angles of deviation the first reflection condition given above is not satisfied closely. This is probably due to their crystals possessing smaller mosaic units than stibnite which appears to have an unusually perfect cleavage.

The conclusion to be derived from the surface diffraction is that there is quite a high absorption of the incident beam as it penetrates the crystal. This must be caused by incoherent, and therefore presumably inelastic, collisions with the atoms of the crystal. The electrons scattered in this way reappear in the remainder of the pattern, which is independent of the direction of the primary beam by virtue of the incoherence produced at the first collision.

[6] Kirchner and Raether, Phys. Zeits. **33**, 510 (1932).

The lines and bands

The lines and bands are space grating effects, agreeing with the conclusion that an electron entering them starts as a spherical wave surrounding a single atom. However, the energy losses at the first collisions must be small compared to the initial energy on account of the sharpness of the pattern.

The pattern appears to stand out in relief, indicating that each Kikuchi line is bordered on one side by a dark strip. The various bands (marked 002, 063, etc.) have dark regions at both edges. In Table II b is the breadth of a band, α its inclination to the horizontal and d the spacing of the corresponding crystal planes obtained from $d = L\lambda/b$. The values of α and d agree with the values calculated from x-ray data. The breadths were measured out to the inner edges of the dark regions, so it seems that these edges, rather than the centers of the Kikuchi lines, mark the Bragg angles.

TABLE II. *Stibnite. Measurements of the bands.*

b (cm)	α	d (A)	X-rays α	X-rays d (A)	(lmn)
1.10	0°	1.95	0°	1.94	002
2.96	22°	0.72	22° 8′	0.72	065
1.80	24°	1.19	24° 30′	1.18	043
2.02	34°	1.06	34° 10′	1.07	063
1.58	45°	1.35	45° 30′	1.36	062
.96	54°	2.23	53° 32′	2.31	041
1.24	63°	1.73	63° 50′	1.72	061

The fact to be explained, then, is that there is increased scattering at angles just larger than the

TABLE I. *Stibnite. Measurements of the spots.*

v (volts)	r_0 (cm)	r_1 (cm)	r_2 (cm)	r_3 (cm)	η (cm)	$\frac{r_1^2-r_0^2}{\eta}$	$\frac{r_2^2-r_1^2}{\eta}$	$\frac{r_3^2-r_2^2}{\eta}$	$\eta v^{\frac{1}{2}}$
19500	2.49	5.78	7.79		0.951	28.7	28.8		133.0
29000	2.20	5.15	6.98	8.32	.770	28.2	28.8	26.5	131.1
39000	1.77	4.55			.650	27.0			128.2
39500	1.75	4.50			.643	26.8			127.8
39800	1.71	4.48	6.12		.637	26.9	27.3		128.1
40000	2.70	5.00	6.50		.632	28.0	27.4		126.3
40800	1.74	4.45	6.10	7.36	.625	26.8	28.0	27.0	126.2
41000	2.97	5.12	6.66	7.90	.632	27.5	29.0	28.4	128.0
42000	1.80	4.55			.636	27.4			130.2
43500	2.20	4.60			.615	26.6			128.2
45000	1.07	3.24	5.88		.614	27.5	27.1		130.1
52500	1.40	4.20	5.80	7.05	.566	27.6	28.2	28.6	129.8
54800	2.36	4.55	6.00	7.14	.553	27.4	27.7	27.1	129.4
58000	1.26	4.05	5.58	6.80	.540	27.4	27.4	28.0	130.0

Bragg angles. From Bethe's theory of elastic reflection by the crystal planes, Shinohara[3] finds this effect but it is too small to account for the observed intensities. We are led, then, to consider the effects of absorption of energy by the thermal vibrations of the crystal. These vibrations can be resolved into a set of independent oscillations which can be excited separately.[7] The interaction energy between an electron and one of the oscillators will be the change in potential energy of the electron arising from a sine wave displacement of the crystal medium. For a long wave oscillator this change in potential will have approximately the same space periodicity as the undisturbed crystal potential. It can then be taken as

$$V=\sum_{lmn} V_{lmn}(t) \exp\left[2\pi i(\mathbf{j}_{lmn}\cdot\mathbf{r})/d_{lmn}\right],$$

where $\mathbf{j}_{lmn}$ is a unit vector normal to the (l, m, n) planes and d_{lmn} is the spacing of these planes. As a first approximation we take an initial plane wave electron $A \exp(2\pi i/h)(\mathbf{p}\cdot\mathbf{r}-p^2t/2m_0)$ of momentum $\mathbf{p}$. The matrix element corresponding to a transition in which the electron's momentum changes to $\mathbf{p}^1$ is different from zero only if $(1/h)(\mathbf{p}-\mathbf{p}')=(1/d_{lmn})\mathbf{j}_{lmn}$. This means that, for absorption of energy by the crystal $(p^2>p'^2)$, scattering only occurs if the glancing angle on the plane (l, m, n) is greater than the Bragg angle $(p^2=p'^2)$. Corresponding to a loss of energy $\delta E=(1/2m_0)(p^2-p'^2)$ the deviation from the Bragg angle is $\delta\theta=(m_0\delta E/hp)d_{lmn}$ so the breadth of the absorption band should be large for large spacings, which is true. The intensity depends on $V_{lmn}(t)$ which in general should increase with d_{lmn}. The absorbed electrons go to form the bright bands and Kikuchi lines contained between pairs of dark bands.

The circles

The well-defined circle in Fig. 1 is surrounded by a narrow dark region, to the right of which appear Kikuchi lines of the group $(1, m, n)$. For $l=1$, the reflection condition $\cos\alpha=\cos\alpha_0-l\lambda/a$ is satisfied only at points lying outside the circle $r_1^{02}=2L^2\lambda/a$. The circle in the photograph, however, is definitely smaller than this. Another circle, too faint to be seen in the reproduction, occurs just inside the circle $r_2^{02}=4L^2\lambda/a$ corresponding to $l=2$. It is much narrower than any Kikuchi line near it, so the circles cannot be considered as envelopes of families of Kikuchi lines. Such envelopes, furthermore, can be shown to be always parabolas.

In Table III, the radii r_1 and r_2 of the two circles are compared with the calculated radii r_1^0 and r_2^0. The other columns give the crystal

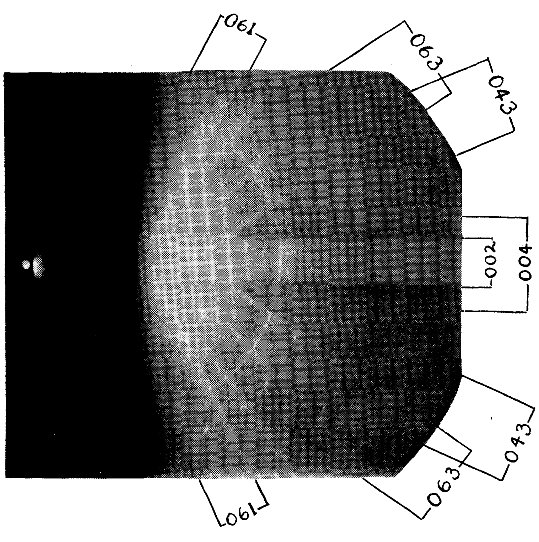

FIG. 1. Stibnite, a axis in plane of incidence.

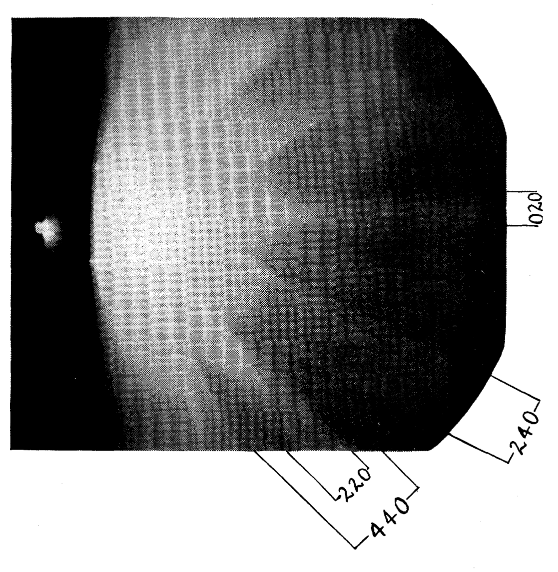

FIG. 2. Galena, cube edge in plane of incidence.

[7] A. H. Wilson, Proc. Roy. Soc. **A138**, 597 (1932).

TABLE III. *Stibnite. Measurements of the circles.*

V (volts)	r_1 (cm)	r_1^0 (cm)	ϕ_1 (volts)	r_2 (cm)	r_2^0 (cm)	ϕ_2 (volts)
18000	5.03	5.14	11	(7.28)	7.26	(−0.3)
27200	4.50	4.65	21	6.50	6.58	13
43700	3.98	4.14	32	5.72	5.85	37
50000	3.87	4.00	30	5.59	5.66	27
53600	3.82	3.93	26	5.45	5.56	42
56200	3.75	3.86	27	5.38	5.46	25

innerpotential ϕ required to deflect the calculated circles into the observed ones. The average value of 26.4 volts is much larger than the usual mean innerpotential of about 10 volts. But, to obtain the one-dimensional diffraction that the circles seem to be, an electron must have its wave packet confined chiefly to a single row of atoms parallel to the a axis. The potential in such a region may be high.

The mechanism whereby an electron wave packet becomes localized may be as follows. The original plane wave electron loses a little energy to an atom and becomes an approximately spherical wave radiating from that atom. If it leaves the atom in a direction nearly parallel to the a axis it may continue in that direction, entrapped in a kind of potential tube. It is scattered finally by the potential variations along the length of the tube.

The parabolas

Towards the right of Fig. 1, and also in Fig. 2 for galena, appear several symmetrical curves which measurements show to be parabolas. They can be explained in a manner similar to that for the circles. This time we imagine an electron confined initially to a *plane* of atoms perpendicular to the c axis. The diffraction will depend only on the atoms in that plane and the reflection conditions are

$$\cos\alpha_0 - \cos\alpha = l\lambda/a,$$

$$\cos\beta_0 - \cos\beta = m\lambda/b.$$

Since $\cos\gamma_0 = 0$ we have $(\cos\alpha + l\lambda/a)^2 + (\cos\beta + m\lambda/b)^2 = 1$. The surfaces determined by this equation meet the photographic plate approximately in a set of parabolas which fit the observed parabolas fairly well. The envelopes of some families of Kikuchi lines, however, are the same set of parabolas. The measurements are not exact enough to indicate whether an abnormal refraction occurs here as with the circles, and so decide which explanation to accept. The continuity of the curves and the correspondence with the case of the circles favor the former.

In conclusion, the writer wishes to thank Professors F. K. Richtmyer and C. C. Murdock for their kind interest in the work and Mr. H. R. Nelson for his valuable collaboration.

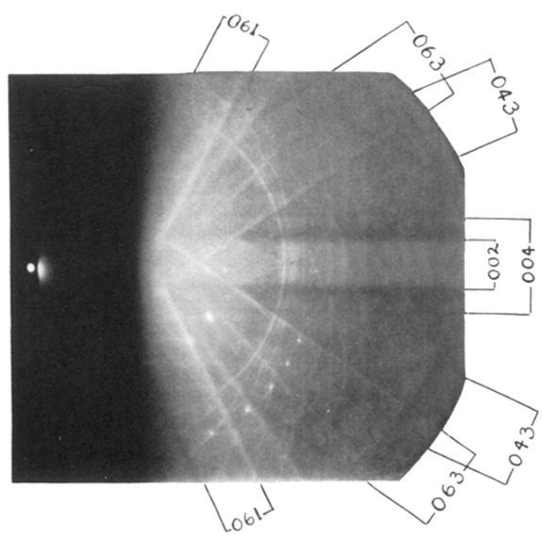

FIG. 1. Stibnite, *a* axis in plane of incidence.

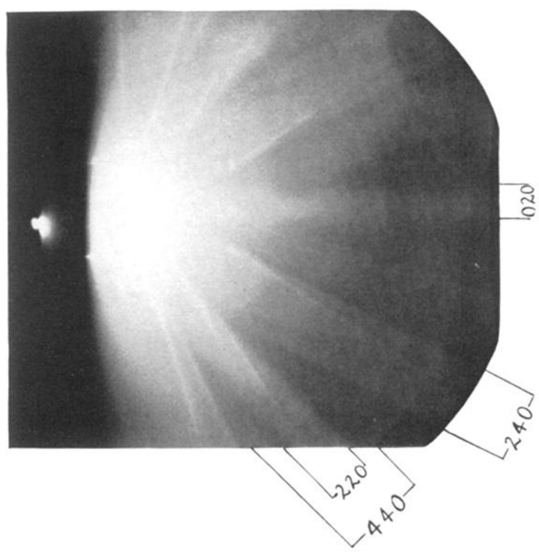

FIG. 2. Galena, cube edge in plane of incidence.