

## Angular dependence of electron-energy-loss spectroscopy: Application to diamond

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New observations of electron-energy-loss spectra for diamond have been made by exploiting the direction dependence of the spectra. The loss peaks known from other workers were present with high intensities. The 23-eV loss peak is attributed mainly to interband transitions, in contrast to other earlier assignments as being mainly due to surface plasmons. The dependence of the loss spectra on direction is interpreted as being due to LEED (low-energy electron diffraction). We suggest that this effect, namely LEED-modulated loss spectroscopy, may be used as a complementary tool for the study of crystalline levels.

### I. INTRODUCTION

Several studies concerning energy levels in diamond have been reported, both theoretical and experimental. Good agreement between theory and experimental results has already been reported a decade ago by Painter *et al.*<sup>1</sup> A major advance in this direction has been made recently by Himpsel *et al.*<sup>2</sup> Using the photon-energy-dependent photoemission technique they determined experimentally by direct measurements some of the energy eigenvalues of diamond at high symmetry points in the Brillouin zone. Nevertheless, there are still much data necessary in order to complete the energy-bands picture.

Following the experimental work of Lurie and Wilson,<sup>3</sup> the present report is on energy-loss spectroscopy on diamond, but with certain improvements and refinements. The method used in this work is direction-dependent energy-loss spectroscopy. The dependence on direction enables one to study loss peaks individually by changing their relative intensities with direction.

We argue that we are observing conventional energy-loss spectroscopy but modulated by LEED (low-energy electron diffraction) in a way similar to the Kikuchi effect<sup>4</sup> which has been observed in LEED studies.<sup>5</sup> We suggest that LEED-modulated loss spectroscopy is a new and simple complementary tool for the examination of crystalline levels.

### EXPERIMENTAL

The measurements were carried out using a VG Scientific system CLAM 100 with its Auger facili-

ties. The electron gun used is their model LEG 61. The incident electron energies ranged from 400 to 900 eV in 100-eV steps. The beam was localized on the sample by using a TV imaging system. Beam current was 20  $\mu$ A. The pressure during the measurement was about  $3 \times 10^{-11}$  mbar.

The analyzer is a 150° spherical sector design, working in the constant analyzer energy mode. The analyzer vessel is constructed in mu metal to provide magnetic shielding. The secondary electrons are collected into the analyzer aperture by a lens. The acceptance angle of the analyzer is determined by the lens aperture and its distance from the sample. In these experiments the electrons collected were those emitted into a cone with apex of 10°, its head on the sample and its base in the lens aperture. Modulation voltage used was 5 V for the Auger spectrum and 8.5 V for the energy-loss spectra.

The sample studied was a type-IIa single-crystal diamond prepared in a similar way to that described by Lurie and Wilson.<sup>3</sup> First it was boiled in oxidizing acids for several minutes, and then washed in demineralized water. Afterwards, the diamond was polished by moving it along a commercial copper surface with 0.25- $\mu$ m diamond powder paste in between. The diamond was moved and pressed against the copper face using finger pressure only, and this procedure was continued for about 15 min. Just before mounting the diamond in the UHV chamber, it was ultrasonically cleaned in acetone and dried by acetone evaporation.

After inserting the sample, the chamber was evacuated for about 20 h including 10 h of bakeout of

the chamber at 200 °C. The diamond was not heated to high temperature *in situ* as this facility was not then available. Since it was not heated, no reconstruction effects were expected.<sup>3</sup> Auger spectra were taken to verify that the sample surface as prepared was in the diamond and not in the graphite state,<sup>3</sup> and to establish the presence of any possible contamination. An x-ray diffraction photograph was taken to establish the crystallographic orientation of the surface. It was found to be nearly (110), namely (861).

Since the geometry of the electron gun and the detector are fixed in the system, the changes in direction were achieved by rotating the crystal using a sample manipulator. The directions of the gun and the detector with respect to the crystallographic axes of the diamond were calculated from the crystal position, from the x-ray diffraction pattern and from their directions in space, using a simple computer program written for this purpose.

The electron-energy-loss spectra were analyzed by computer. In the analysis, the spectra were numerically reconstructed assuming a Gaussian lineshape for the peaks. The smallest number of lines possible was taken to fit the reconstructed to the experimental curves. The variable parameters were the energies, the intensities, and the widths of the lines.

## RESULTS

In describing the following spectra, we use the coding of Lurie and Wilson<sup>3</sup> to identify specific structure details. The Auger spectrum for the range 80–300 eV is given in Fig. 1. The features of this spectrum fit those given by Lurie and Wil-

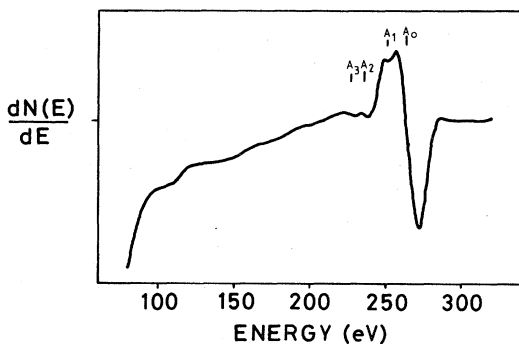


FIG. 1. Auger spectrum of diamond. The coding of peaks follows that of Lurie and Wilson Ref. 2. Beam energy 3 kV, current 20  $\mu$ A, modulation voltage 5 V.

son<sup>3</sup> which confirms that the sample surface is in the diamond phase.

Another Auger spectrum was taken for the energy range of 200–1200 eV (not given here). No detectable contamination was seen above the baseline noise level, which represented a maximum of 3% of the carbon peak height. The electron-loss spectra were taken for several sample orientations, for different energies of the primary beam, and for different modes of the electron beam.

Figure 2 shows the difference between the energy-loss spectrum using a beam about 20  $\mu$ m in diameter and that obtained by scanning with the same beam a 10 times larger area of the diamond surface. In both spectra one sees loss peaks with different relative intensities to those given in Lurie and Wilson.<sup>3</sup> An interesting observation is that the relative intensities change with the incident beam modes.

We define the azimuthal angle  $\phi$  as a rotation of the diamond about an axis normal to the diamond surface, and the tilt angle  $\theta$  as a rotation of the diamond about an axis parallel to the surface. In Fig. 3 the dependence on  $\theta$  is demonstrated for a change in angle of 2°.

In Fig. 4 spectra for different azimuthal angles are given. Analyzing the spectra of Figs. 3 and 4, good fits were achieved between the reconstructed and experimental curves, using the same six loss peaks having different intensities in each case. The line width was kept the same for all the loss peaks but for the peak  $P_7$  (due to double loss to bulk plasmons), which was found to be broader.

The elastic peak was fitted by a linewidth narrower than that of the loss peaks. The linewidths were found to be 12 eV for five of the loss peaks,

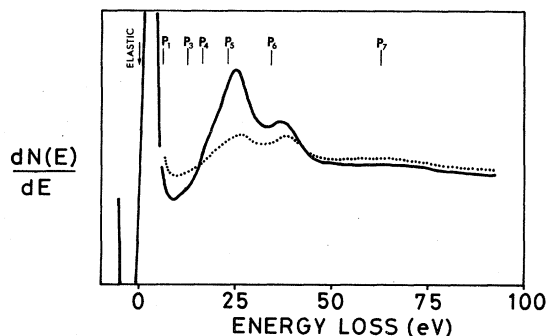


FIG. 2. Energy-loss spectra of diamond type-IIa with face (861). Beam energy 600 eV, current 20  $\mu$ A, modulation voltage 8.5 V. Solid line, scanned beam; dotted line, unscanned beam. Amplifier sensitivity for solid line compared to that for the dotted line is  $\frac{3}{10}$ .

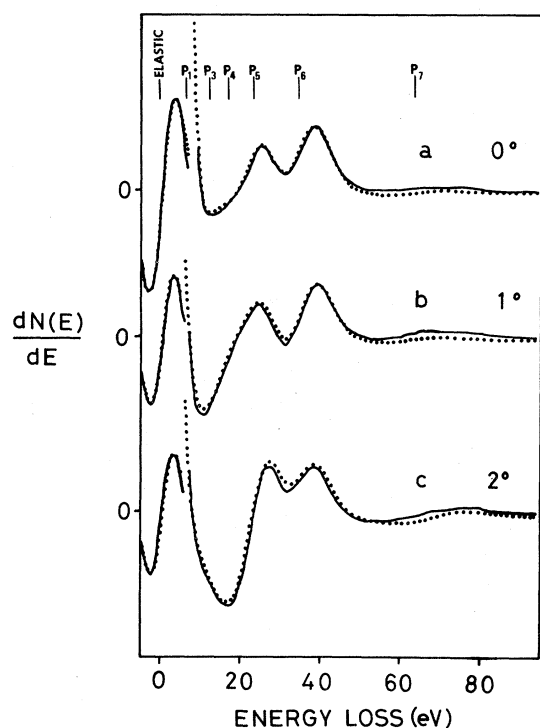


FIG. 3. Energy-loss spectra of diamond type-IIa with face (861) for different tilt angles  $\theta$ . The relative changes  $\Delta\theta$  in the tilt angle are given in the figure for the different spectra. The relative sensitivity of the amplifier was 1 for the loss peaks in *a*, *b*, and *c*,  $\frac{1}{30}$  for the elastic peaks in *a*, and  $\frac{1}{10}$  in *b* and *c*. Beam energy 600 eV, modulation voltage 8.5 V. Solid lines, experimental spectra; dotted lines, reconstructed spectra.

17 eV for  $P_7$  and 7 eV for the elastic peak. Tables I and II give the peak intensities for the two sets of spectra (Figs. 3 and 4) as well as their energies. Since the absolute intensities must depend on the experimental geometry, the relative intensities are given. In doing so, the intensity of the well-known loss peak due to bulk plasmons ( $P_6$ ) was normalized to 1. The reason is that among the high-intensity peaks, this peak is the most unlikely to depend on direction. This point will be considered later in the discussion.

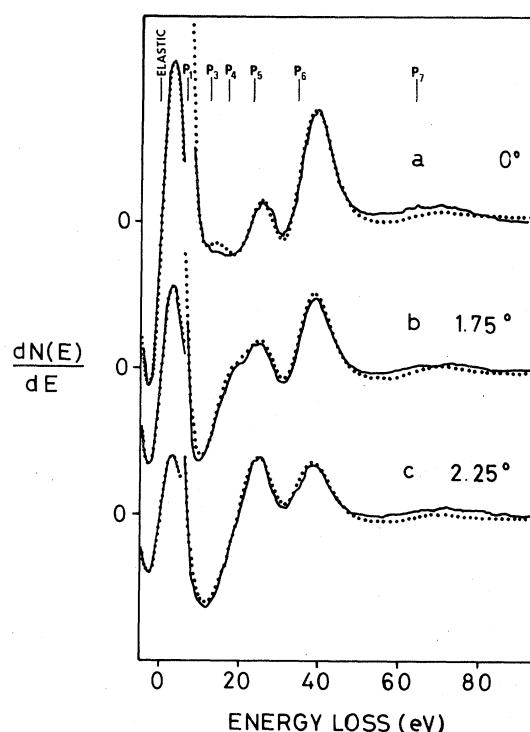


FIG. 4. Energy-loss spectra of diamond type-IIa with face (861) for different azimuthal angles  $\phi$ . The relative changes  $\Delta\phi$  in the azimuthal angle are given in the figure for the different spectra. The relative sensitivity of the amplifier was 1 for the loss peaks in *a*, *b*, and *c*,  $\frac{1}{30}$  for the elastic peaks in *a*, and  $\frac{1}{10}$  in *b* and *c*. Beam energy 600 eV, modulation voltage 8.5 V. Solid lines, experimental spectra; dotted lines, reconstructed spectra.

Following the variation of line intensities with sample orientation one can clearly see how the peaks progressively change. In Fig. 4, for example, spectrum *a* ( $\Delta\phi=0^\circ$ ) has the highest elastic and  $P_1$  peaks among the three spectra. Going from *a* ( $\Delta\phi=0^\circ$ ) through *b* ( $\Delta\phi=1.75^\circ$ ) to *c* ( $\Delta\phi=2.25^\circ$ ) the elastic peak and the 6.5-eV peak  $P_1$  decrease, the 12.5-eV peak  $P_3$  first increases and then decreases, and the peaks  $P_4$  with 16.5 eV and  $P_5$  with 23 eV increase monotonically throughout.

TABLE I. Relative intensities ( $\pm 10\%$ ) of peaks appearing in Fig. 3.

Peak	Elastic	$P_1$	$P_3$	$P_4$	$P_5$	$P_6$	$P_7$
Energy loss (eV)	0	$6.5 \pm 1.0$	$12.5 \pm 0.5$	$16.5 \pm 0.8$	$22.7 \pm 0.8$	$34.0 \pm 0.5$	$63 \pm 2$
<i>a</i>	75	0.71	0.93	0.43	1.36	1	.05
<i>b</i>	21	0	0.90	0.41	1.1	1	.05
<i>c</i>	22	0	0	0.64	1.9	1	.05

TABLE II. Relative intensities ( $\pm 10\%$ ) of peaks appearing in Fig. 4.

Peak	Elastic	$P_1$	$P_3$	$P_4$	$P_5$	$P_6$	$P_7$
Energy loss (eV)	0	$6.5 \pm 1.0$	$12.5 \pm 0.5$	$16.5 \pm 0.8$	$22.7 \pm 0.8$	$34.0 \pm 0.5$	$63 \pm 2$
<i>a</i>	83	0.17	0.46	0.09	0.88	1	0.05
<i>b</i>	20	0	0.72	0.63	0.94	1	0.05
<i>c</i>	20	0	0.33	1	1.5	1	0.05

The changes between the different graphs in Figs. 3 and 4 occur for changes in directions of only about  $2^\circ$ . We can deduce from this, that the angular linewidth is about  $2^\circ$ . This is not inconsistent with the  $10^\circ$  cone detector acceptance, since the observations are made with reference to the rotation of the crystal specimen and are directly sensitive therefore to the criteria for the Bragg conditions which are defined within  $2^\circ$ . The dependence upon the energy is shown in Fig. 5 with beam energies 600, 700, and 800 eV. For 600 eV the 23-eV loss peak  $P_5$  is higher than the 34-eV peak  $P_6$ , while the inverse is found for 700- and 800-eV incident electron energy.

One should note also the 115-eV loss peak appearing in Fig. 5 for 700-eV incident energy (spectrum *b*). Both the intensity and the energy of this peak are sample-direction dependent. The energy changes over a range of about 20 eV, i.e., its energy is in the range  $120 \pm 20$  eV, depending on the direction. In the discussion this phenomenon will be considered in order to substantiate our general conclusions.

It should be emphasized that the observed effects are not artifacts coming from changing distances between crystal and detector or gun, or caused by magnetic field affecting the electrons. The spectra were not sensitive to translational movements while they are very sensitive to sample directional changes. As mentioned earlier, the analyzer is magnetically shielded by its mu metal vessel, so that no magnetic field interference is found.

## DISCUSSION

Before discussing the results one has to realize that the observed peaks are not Auger peaks with energies in the range of  $580 \pm 10$  eV. Were they Auger peaks, they would have to be attributed to chemical elements like Ba and Mn which were unlikely to be found on the diamond surface. Nor is it possible to interpret the peaks as due to an oxy-

gen Auger peak with its energy shifted by  $\sim 70$  eV due to surface charging. Such high shifts were not observed while taking the above spectra. Although for 700-eV beam energy [Fig. 5(b)] a broad line having 585-eV energy (loss peak of 115 eV) appears, yet no such line occurs for 800-eV beam energy [Fig. 5(a)]. Finally, Auger peaks are not as sensitive to direction changes as was found to be the case for the observed peaks. It is therefore concluded that these peaks are loss peaks.

Another important point is the beam mode dependence of the spectra, demonstrated in Fig. 2.

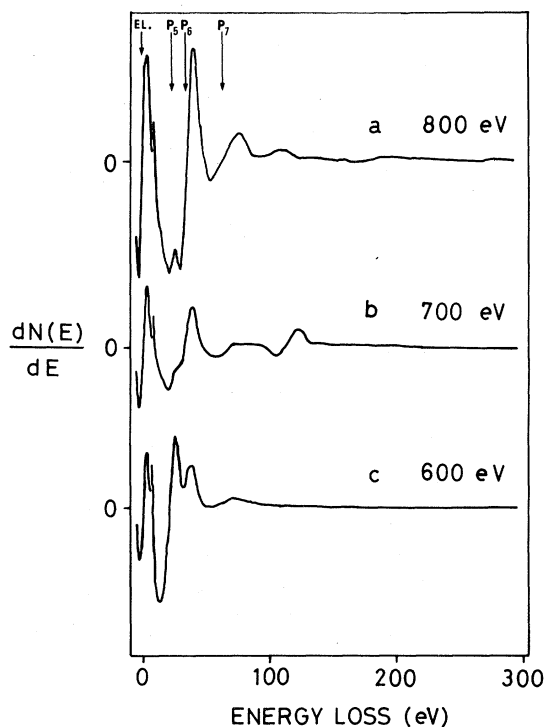


FIG. 5. Energy-loss spectra of diamond type-IIa with face (861) for different beam energies and the same direction conditions. The different energies are given in the figure for each graph. The relative sensitivity of the amplifier was 1 for the loss peaks and  $\frac{1}{10}$  for the elastic peaks in *a*, *b*, and *c*.

This dependence might be attributed to extreme electron-beam damage from a stationary beam as compared to a scanning beam. Such an effect has been reported by Pepper,<sup>6</sup> who observed differences in fine structure of ionization loss spectra as well as of Auger spectra for diamond, taken with the diamond stationary under the electron beam and with the diamond moving at 7  $\mu\text{m}/\text{sec}$ .

One should bear in mind, therefore, the possibility of electron-beam damage although we have no firm evidence in support thereof. In discussing the results, two aspects will be considered. The first aspect attributes the peaks to different processes occurring in the crystal, following earlier work. In the second part we deal with the direction-dependence.

#### Loss processes

The energies of all peaks given in Tables I and II agree within the limits of accuracy with the values found by other workers.<sup>1-3,7,8</sup> Peak  $P_1$  at 6.5 eV is assigned to the  $\Gamma'_{25} \rightarrow \Gamma_{15}$  transition. This assignment is based on the findings of Roberts and Walker<sup>7</sup> and Himpsel *et al.*,<sup>2</sup> who used different methods to determine electronic transitions and electronic levels in the energy bands of diamond. Roberts and Walker<sup>7</sup> carried out measurements of diamond optical reflectance and from the features of these spectra made deductions about the electronic transitions and electronic levels. They found a peak at 7.3 eV which they attributed to the transition  $\Gamma'_{25} \rightarrow \Gamma_{15}$ . Himpsel *et al.*<sup>2</sup> utilized the photon-energy-dependent photoemission techniques to determine electronic energy levels of diamond. They determined the critical point  $\Gamma_{15}$  to be 6.0 eV above  $\Gamma'_{25}$ . According to Lurie and Wilson<sup>3</sup> the peak  $P_1$  is found to have energies between 5 and 7.3 eV depending on the experimental conditions. Therefore, the energy of 6.5 eV found in the present work matches the earlier findings and  $P_1$  can indeed be attributed to the transition  $\Gamma'_{25} \rightarrow \Gamma_{15}$ .

The  $P_3$  peak at 12.5 eV is assigned to several electronic transitions between crystalline levels such as  $\Sigma_2 \rightarrow \Sigma_3$ ,  $L'_3 \rightarrow L_3$ ,  $X_4 \rightarrow X_1$ , and  $L'_3 \rightarrow L_1$  (see Refs. 1 and 3).  $P_4$  at 16.5 eV can be attributed to the  $X_1 \rightarrow X_1$  transition,<sup>7</sup> but according to the findings of Himpsel *et al.*<sup>2</sup> it would be due to the  $\Gamma'_{25} \rightarrow \Gamma'_2$  transition giving a  $15.3 \pm 0.5$ -eV photoelectron peak in their work. We may note that experimental accuracy does not permit one to distinguish which of these two possibilities is correct.

In the present work, the peaks  $P_3$  and  $P_4$  are

relatively intense compared to those achieved by Lurie and Wilson<sup>3</sup> but our result is in good agreement with the findings of Roberts and Walker,<sup>7</sup> Himpsel *et al.*<sup>2</sup> (for peak  $P_4$ ), and the theoretical estimation of Painter *et al.*<sup>1</sup> (for  $P_3$ ). The peak  $P_5$  would be attributed according to Roberts and Walker<sup>7</sup> to the transition between the crystalline levels  $\Gamma'_{25}$  and  $\Gamma_1$  or to an extrinsic transition due to contamination. Lurie and Wilson<sup>3</sup> assign  $P_5$  to the  $\Gamma'_{25} \rightarrow \Gamma_1$  transition and to loss to surface plasmons.

According to Maguire<sup>8</sup> the 23-eV peak  $P_5$  cannot be assigned to the  $\Gamma'_{25} \rightarrow \Gamma_1$  transition since it is forbidden from symmetry considerations. He attributes it to surface plasmons. Strong support in favor of  $P_5$  being due to interband transition and not to surface plasmons is given by Himpsel *et al.*<sup>2</sup> They found a direct electron transition from  $\Gamma'_{25}$  to a band at  $\Gamma$  which is  $24.0 \pm 1.5$  eV higher than  $\Gamma'_{25}$ . They argue that this  $\Gamma$  state consists possibly of two unresolved  $\Gamma$  points of unknown symmetry. This experimental finding suggests that there is an existing interband transition with transition energy at about 23 eV. It is most probably this transition or these transitions which add  $P_5$  to the loss peaks.

With regard to intensities, the peak  $P_5$  is much more intense here than in the data of other workers who have made energy-loss-spectroscopy measurements. Indeed, for certain crystallographic directions it is higher than expected from a surface-plasmon peak relative to a bulk-plasmon peak.

Himpsel *et al.*<sup>2</sup> do not identify the upper level  $\Gamma$  to which the transition  $\Gamma'_{25} \rightarrow \Gamma$  takes place, giving a 24-eV photoemission peak. As pointed out before, Maguire<sup>8</sup> excludes the possibility of  $\Gamma$  being  $\Gamma_1$  since  $\Gamma'_{25} \rightarrow \Gamma_1$  is a forbidden dipole transition. Although  $\Gamma'_{25} \rightarrow \Gamma_1$  is a forbidden dipole transition, it is an allowed quadrupole transition. Since for 600 eV the electron's wavelength is 0.49  $\text{\AA}$  the quadrupole interaction between the incoming electron and the atomic electrons is significant. Also, there are allowed dipole transitions between levels close to  $\Gamma'_{25}$  and  $\Gamma_1$  having  $0 < |\vec{k}| \ll 2\pi/a$  ( $\vec{k}$  is the wave vector,  $a$  is the lattice constant) which involve a large number of electronic states. According to the energy band structure calculated by Painter *et al.*<sup>1</sup> the lines extending from  $\Gamma'_{25}$  have a shallow maximum, and those extending from  $\Gamma_1$  have a shallow minimum. It follows that the density of states along the lines close to  $\Gamma'_{25}$  and  $\Gamma_1$  is high. The allowed dipole transitions between these  $\Delta$ ,  $\Lambda$ , and  $\Sigma$  lines are the following:  $\Delta_5 \rightarrow \Delta_1$ ,  $\Lambda_3 \rightarrow \Lambda_1$ ,  $\Lambda_1 \rightarrow \Lambda_1$ ,  $\Sigma_1 \rightarrow \Sigma_1$ ,  $\Sigma_2 \rightarrow \Sigma_1$ , and  $\Sigma_3 \rightarrow \Sigma_1$

(see Ref. 8 and Tables 2.10 and 2.18 of Ref. 9).

Hence there are several allowed dipole transitions with high probability and with energy close to the energy difference between  $\Gamma'_{25}$  and  $\Gamma_1$ . One should also take into account the umklap process which has high probability for the beam energies used here. The umklap process would enhance the transition probability between the above-mentioned levels.

In conclusion for  $P_5$ : The direct experimental evidence of a transition  $\Gamma'_{25} \rightarrow \Gamma$  with 24-eV transition energy found by Himpsel *et al.*<sup>2</sup> and the high intensity achieved in the present work for  $P_5$ , both prove that  $P_5$  is due mainly to interband transitions and not to surface plasmons. The theoretical considerations suggest that the transitions are  $\Gamma'_{25} \rightarrow \Gamma_1$  and "neighboring" levels in the  $\vec{k}$  space, along the lines  $\Delta$ ,  $\Lambda$ , and  $\Sigma$ .  $P_6$  and  $P_7$  are assigned to loss to one and two bulk plasmons, respectively.<sup>3,8</sup>

#### Direction dependence

Let us now consider the directional dependence of the loss spectra: The dependence of the peaks' intensities on direction and energy implies that diffraction effects are involved. It is known from electron microscopy that inelastically scattered electrons can diffract after an additional elastic scattering before leaving the crystal. This is of course the Kikuchi effect,<sup>4</sup> which has been observed also in LEED studied, e.g., Ref. 5. The range of incident energies used here is from 100 to 1000 eV; therefore only the surface is probed by the beam and only diffraction due to the surface symmetry can be involved. It is thus the LEED considerations that should be used there, and the theory relevant is that which has been described by Pendry.<sup>10</sup> Finding LEED effects here should not be a surprise since diamond is known to be special in that it is easy to get a good LEED surface (which is not the case with metals). It is of course essential to confirm that the directions of the gun and detector relative to the crystal symmetry axes fulfill the Bragg conditions for diffraction.

The crystal orientation is derived from the diamond x-ray diffraction pattern. As mentioned earlier in the experimental section, the diamond face was close to (110), namely (861). The plane (861) is inclined at a shallow angle to the (110) face. It cuts the (110) planes in lines which are in the  $[1\bar{1}2]$  direction. In this way the diamond surface can be looked at as composed of steps having the (110)

face. Those steps are "infinitely" long in the  $[1\bar{1}2]$  direction; they are about 4 lattice constants wide, and they are  $2^{-1/2}$  lattice constants high. Treating the diamond surface as (110) for the LEED calculation will lead to an error in the LEED signal intensity, arising from the edges of those steps. Nevertheless, since the steps are wide enough there will be a net of constructive diffraction whenever Bragg conditions are fulfilled for the (110) face. The system of axes chosen for the LEED calculations is composed of  $x$  axis in the [001] direction,  $y$  axis in the  $[1\bar{1}0]$ , and  $z$  axis in the [110] direction.

In this system the (110) face unit cell is given by the vectors

$$\vec{a} = (a_x, a_y, a_z) = a(1, 0, 0),$$

$$\vec{b} = (b_x, b_y, b_z) = a(0, 2^{-1/2}, 0),$$

where  $a = 3.57 \text{ \AA}$  is the diamond lattice constant. The reciprocal lattice of the (110) face will then be built from the vectors

$$\vec{A} = \frac{2\pi}{a}(1, 0, 0),$$

$$\vec{B} = \frac{2\pi}{a}(0, \sqrt{2}, 0).$$

Under the experimental conditions used, the accuracy of the absolute values of the measured and calculated angles is determined to within about  $\pm 2^\circ$  only. On the other hand, the changes in the angles are determined to within  $\pm 0.1^\circ$  for  $\theta$  and  $\pm 0.05^\circ$  for  $\phi$ . The calculated angles between the different elements involved are given in Table III.

With these directions, one can calculate the Bragg conditions for the electron beam with 600-eV energy. These calculations show that when taking the loss spectra, Bragg conditions for constructive diffraction are fulfilled within the experimental accuracy. In particular one finds that the appropriate scattering vector is

$$\vec{g} = (3\vec{B} - 5\vec{A}) \pm 3\%.$$

This means that the detector is for these conditions

TABLE III. Angles between different elements in degrees.

	Gun	Detector	[110]	$[1\bar{1}0]$	[001]
Gun	0	36	41	56	69
Detector	36	0	22	88	69
[110]	41	22	0	90	90
$[1\bar{1}0]$	56	88	90	0	90
[001]	69	69	90	90	0

in a diffraction maximum direction of the elastically scattered beam or just off-maximum. In this situation it is quite reasonable to conclude that by rotating the sample slightly, one will get off the maxima of the elastic peaks in the diffraction pattern, and get maxima of inelastic peaks with slightly different energy, in accordance with the usual Bragg conditions.

We have mentioned earlier that the angular line widths of the loss peaks are about  $2^\circ$ , which is the order of magnitude found in LEED for the line width.<sup>11,12</sup> All of these considerations support the relevance of LEED to the directional effects, as observed. The next test that can be posed is whether the peaks' intensities follow the Bragg condition precisely with a change in direction. Considering all the peaks but  $P_6$  and  $P_7$  one sees in Fig. 4, for example, the change in their intensity with  $\phi$ . For the given experimental conditions a change of  $1^\circ$  in direction will change the cosine by 2–4% depending on the angle. The change of the electron wavelength from the elastic peak to the inelastic peaks is 1–2%. The changes in Bragg conditions occurring in Fig. 4 due to the direction changes are therefore largely compensated by changes in the wavelength of the different loss peaks. Regarding the correlation between the peaks' maximum and the direction, it has already been argued in connection with Fig. 4 that the peaks' intensities change in the correct sequence as expected. It was mentioned already that the peak  $P_6$  is most unlikely to show a diffraction effect. The same applies to  $P_7$ . The question thus arises as to why on the other hand the other peaks do diffract. There will be a higher probability for the diffraction effect of the inelastically scattered electrons if the inelastic scatterers are distributed with the crystal periodicity than if they are randomly distributed. The reason is that the coherency of the primary beam can be conserved in the former case better than in the latter. The peaks  $P_1$ ,  $P_3$ ,  $P_4$ , and  $P_5$  come from inelastic scattering by electrons with wave functions having the crystalline order, and perhaps by surface plasmons which are created always in the surface and have one direction (perpendicular to the surface). The loss peaks  $P_6$  and  $P_7$  due to bulk plasmons are mainly composed of incoherent electrons, since the bulk plasmons may occur at any spatial point. Part of these electrons may, of course, also be coherent. This can explain why the diffraction is observed mainly in the  $P_1$ ,  $P_3$ ,  $P_4$ ,  $P_5$ , and elastic peaks and only very slightly in  $P_6$  and  $P_7$ .

A possible explanation for the peak appearing at

115 eV for 700-eV beam energy (Fig. 5) is as follows: The primary electrons with 700-eV energy may lose energy in several steps in different ways; they may excite several times different electrons to different levels in different order. The spectrum resulting from this process will be composed of resolved lines distinguished from the background, because of a few preferred transitions, e.g., those giving the 12.5-eV loss peak. Some of those lines might have an energy of  $580 \pm 20$  eV. In other words, there will be loss peaks of  $120 \pm 20$  eV. The electrons which suffered an energy loss of 120 eV are already deep enough in the crystal and can be detected only by enhancement caused, for example, by diffraction. Figure 5 was taken in the directional conditions so as to give a diffraction maximum to  $P_4$  and  $P_5$ . This means that coherent electrons having energy of about 580 eV [(600–23) eV and (600–17) eV] will diffract constructively. Therefore, electrons originating in the 700-eV beam and left with  $580 \pm 20$ -eV energy can now diffract and enhance the peak 585 eV (loss peak 115 eV for 700-eV beam). It is also understood now how the energy of this peak changes with the direction. The peak is thus composed of several peaks close in energy. As the direction changes, the Bragg conditions change and each time a different peak will satisfy Bragg conditions for its own maximum. It does not occur for a beam energy of 800 eV because the electrons must then go too deep into the crystal to lose energy from 800 down to 580 eV.

## SUMMARY

Energy-loss spectra determined in this work show the known 12.5- and 23-eV peaks with high intensities. Peaks with energies 6.5 and 16.5 eV are also found with high intensities. All four peaks show diffraction behavior. The energies of the lines as derived from the experimental spectra agree well with other measurements. The high intensity of the 23-eV peak achieved here and the finding of interband transitions with energy  $24.0 \pm 1.5$  eV in photoemission studies we argue prove that the 23-eV loss peak is due mainly to interband transitions and not to surface plasmons. The high intensity of the 12.5-eV peak measured here is in good agreement with optical work and with the theory. The energies and intensities of the 6.5- and 16.5-eV peaks agree with conclusions from optical studies as well as from photoemission studies of diamond.

The different lines could be observed at high intensity due to their directional dependence, attributed here to the diffraction effect. This effect is suggested as a new complementary tool for the study of crystalline levels, i.e., using loss spectroscopy modulated by LEED one can separate the individual loss peaks, and detect peaks which otherwise would be lost in higher peaks or in the background.

To exploit this effect it is recommended that a primary beam energy in the range of several hundred eV be used in order to avoid the range of Bloch waves coming out of the crystal.<sup>10</sup> These Bloch waves have energy of the order of 100 eV, and may interfere with the backscattered electrons and complicate the loss spectra if a primary beam energy of 100-eV order of magnitude is used.

We recommend strongly that the scanning beam mode be used to achieve high intensity of the diffraction effect since in the stationary beam condition we find much weaker peaks. The reason for

this difference is not yet understood but it might be attributed to damage or reconstruction of the surface under stationary beam conditions when some critical beam current is exceeded.

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