

HREELS scattering mechanism from diamond surfaces

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Interpretation of high-resolution electron-energy-loss (HREEL) spectra is dependent on knowledge of the applicable selection rules and therefore on the scattering mechanism involved. HREEL spectra from hydrogen-terminated C(100) demonstrate that impact scattering is the dominant mechanism and that dipole selection rules are not valid on this surface. We discuss reasons for the dominance of impact scattering and implications for the interpretation of HREEL spectra from diamond.

INTRODUCTION

The chemical vapor deposition (CVD) of diamond offers diverse technological applications. Several recent reviews,¹⁻⁴ books,⁵⁻⁷ and conference proceedings⁸ offer excellent summaries of these reasons for interest in the CVD of diamond. However, many aspects of the surface structure, electronics, and chemistry are not yet understood. High-resolution electron-energy-loss spectroscopy (HREELS) has recently been applied to investigations of the diamond surface and its chemistry.⁹⁻¹⁷ Waclawski *et al.*⁹ studied a hydrogen-exposed C(111) surface and reported a single peak in the CH stretching region of the spectrum but a doublet in the bending region. They interpreted these results as indicating CH₃ termination of the (111) diamond surface. Sun and co-workers¹¹⁻¹⁴ used HREELS to study both (100)- and (111)-oriented polycrystalline diamond films following growth by filament-assisted CVD. On (111) faceted samples, a single CH stretching mode was observed while either one or multiple bending modes were observed after growth under various conditions. HREEL spectra from (100)-oriented films always showed multiple CH bending modes that were assigned to CH₂ moieties. Lee and Apai¹⁰ observed a single feature in the CH stretching region and a single feature in the CH bending region on C(100) and C(111). Using peak-deconvolution techniques, they assigned the spectra to multiple CH_x ($x=1-3$) species of both sp^2 and sp^3 bonded carbon. Aizawa *et al.*¹⁵ found multiple CH stretching modes in HREEL spectra collected off specular from C(111) in addition to several vibrational peaks in the CH bending region. On C(100), they observed only one stretching mode and one prominent bending vibration. The authors of this paper have observed a single peak in the CH stretching region and a single peak in the CH bending region in HREEL spectra from hydrogen-terminated polycrystalline diamond¹⁶ and C(100).¹⁷

Sun *et al.* used the dipole selection rule in interpreting their results from polycrystalline diamond films and posed the question "Is the selection rule not valid?"¹² Aizawa *et al.* assumed dipole selection rules to interpret specular and off-specular HREELS data.¹⁵ In this paper we examine the validity of dipole selection rules in HREELS from hydrogen-terminated C(100). We report

experimental evidence that vibrational excitation by dipole scattering from hydrogen-terminated diamond occurs only on extremely smooth surfaces. Even in this case, losses due to both impact and dipole scattering are observed in specularly scattered electrons. In addition, we propose an explanation for the dominance of impact scattering in the HREEL spectra from hydrogen-terminated diamond surfaces.

EXPERIMENTAL PROCEDURES

Experiments were performed in an ion, titanium-sublimation and turbo-molecular pumped stainless-steel (UHV) chamber¹⁶ with a base pressure of 2×10^{-10} Torr. The sample was mounted by means of Ta wires to a Ta disk. The disk was mounted on a tantalum puck that could be removed from or reintroduced into the UHV chamber via a load-lock chamber, which achieved a base pressure of 2×10^{-7} Torr. Sample heating was achieved with electron bombardment of the Ta disk from the back side. The temperature of the Ta disk near the sample was measured with a Chromel-Alumel thermocouple. The sample temperature was also measured with a single-color (0.8–1.1 μm) optical pyrometer for temperatures above 600 °C and found to agree with the thermocouple measurements to within 30 °C at 1000 °C for an emissivity setting of 0.24. However, thermocouples attached to a metal sample mount have recently been shown to measure a higher temperature than the actual temperature of the diamond sample.¹⁸

HREEL spectra were acquired with a 127° cylindrical monochromator and analyzer (LK Instruments, Model LK2000) using electron energies of 6–14 eV and incident direction 60° from the surface normal. The spectra were collected with the spectrometer resolution set to 40 cm^{-1} , however, resolution of 60–100 cm^{-1} were typically attained. The sample was maintained at room temperature for all spectra reported here.

The single-crystal diamond sample used in this study was a boron-doped synthetic diamond.¹⁹ A 3×3-mm² (100) face was used for all surface investigations. The sample was cleaned by boiling for 15 min in 3 HCl:1 HNO₃ and for 15 min in 3 H₂SO₄:2 HNO₃ and rinsed in deionized water. This was followed by an *ex situ* exposure to a microwave-generated hydrogen plasma at a sample temperature of 800 °C. We have observed that the

plasma treatment produces an extremely smooth, hydrogen-terminated C(100) surface.²⁰ This surface is stable in air and following introduction into UHV, Auger-electron and energy-loss spectroscopy showed the samples were free of surface contaminants and sp^2 carbon. No adsorbed hydrocarbons were observed, unlike acid-cleaned surfaces.¹⁶

Low-energy electron diffraction (LEED) of hydrogen-terminated C(100) yielded either a 1×1 or a two-domain 2×1 pattern, depending on surface smoothness. In addition, the lowest incident electron energy at which LEED spots were observed was not always the same. For a surface that had been acid cleaned, then heated and H atom dosed in vacuum, a 1×1 LEED pattern was visible at electron energies of 70 eV or above. After the initial 1.5-h hydrogen plasma treatment, a sharp, 2×1 LEED pattern was observed at energies as low as 35 eV. This surface will be referred to in the rest of this paper as surface *A*. Following several subsequent plasma treatments totaling 4.5 h, half-order spots were visible at energies as low as 13 eV. This surface will be referred to in the rest of this paper as surface *B*. The decrease in the energy at which the half-order LEED spots were observed is interpreted as indicating production of larger and less defected domains, i.e., a smoother surface. Furthermore, the surface producing the LEED spots at 13 eV, surface *B*, is assumed to be smoother than the surface yielding spots only at 35 eV and above, surface *A*. HREEL spectra were acquired from both surfaces *A* and *B* in order to compare the effect of smoothness on the scattering mechanism.

RESULTS

Figure 1 shows a HREEL spectrum acquired from surface *B*, that is, C(100) after 4.5 h of *ex situ* hydrogen plasma treatment. The spectrum was collected in the specular direction with an incident electron energy of 11.5 eV. Spectra from surface *A* were similar, except for a decreased intensity of the elastic peak relative to the loss region. Spectra acquired following heating to $\leq 900^\circ\text{C}$ and/or *in situ* exposure to hydrogen atoms produced by a heated W filament were also similar to the spectrum in Fig. 1 and are therefore not shown. The spectra exhibit a narrow, symmetric peak at 2920 cm^{-1} that has been assigned to a CH stretching vibration.^{15,17} A slightly wider and asymmetric peak is observed near 1250 cm^{-1} and has been assigned to a CH bending vibration.^{10,15} Lee and Apai¹⁰ have observed a mode at 1220 cm^{-1} on the hydrogen-free surface and have assigned it to a surface phonon. Recently, we have also observed a substrate vibration near 1220 cm^{-1} and have seen that this mode contributes to the intensity of the peak near 1250 cm^{-1} in the spectra of the hydrogen-covered surface.¹⁷ Broad peaks are also present near 2440 and 3600 cm^{-1} and we assign them to multiple losses or overtones of the modes(s) near 1250 cm^{-1} . Further discussion of the assignments of these vibrational modes and those observed on the deuterated surface will be published elsewhere.¹⁷ In this paper, the vibrational peaks will be referred to by their peak position in the HREEL spectrum.

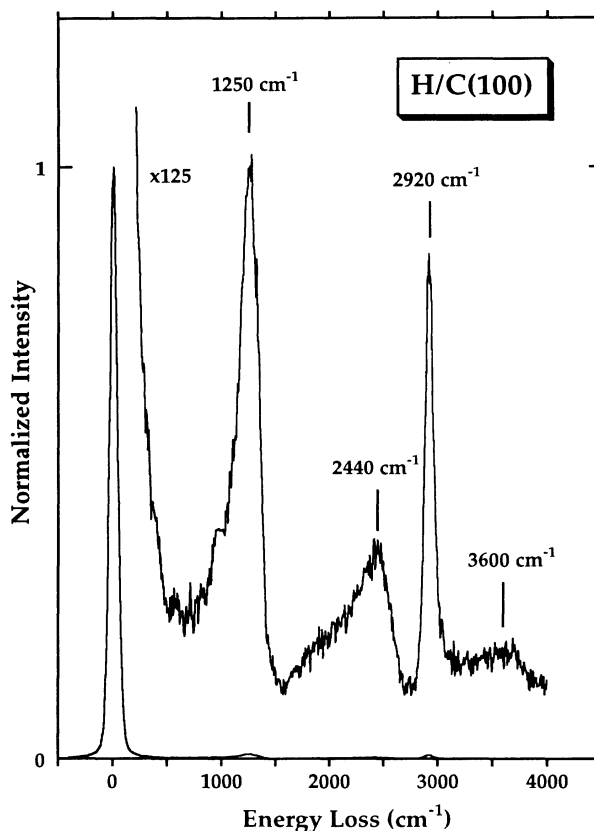


FIG. 1. High-resolution electron-energy-loss spectrum of H-saturated C(100). The spectrum was collected in the specular direction with an incident energy of 11.5 eV. The full width at half maximum of the elastic peak is 85 cm^{-1} .

HREEL spectra were acquired as a function of incident electron energy from 7 to near 14 eV. Since the loss features have an angular dependence different than that of the elastic peak, normalization to the elastic intensity would yield integrated intensities that were very sensitive to tuning. Normalization to the intensity of the background in the same region of the spectrum as the loss feature eliminates the effects of changes in spectrometer tuning as the incident electron energy is changed. Therefore, to normalize the intensity of the loss features at 1250 , 2440 , and 2920 cm^{-1} , a line was fit to the background in the vicinity of the loss peak. The loss features were then normalized by dividing the integrated intensity of the loss peak (after subtraction of the linear background) by the integrated intensity of the background. Figure 2 shows the integrated intensities of the three vibrational features normalized to the background versus incident electron energy. The intensity of the CH bend and its first overtone appears independent of incident energy, while the CH stretch shows a smooth increase in intensity above an incident energy of about 9 eV.

HREEL spectra were acquired as a function of collection angle without changing spectrometer tuning or sample position. The absolute count rates for the elastic peak and loss peaks at 1250 , 2440 , and 2920 cm^{-1} were integrated over the width of the peak after a linear background subtraction. Figure 3 shows the integrated inten-

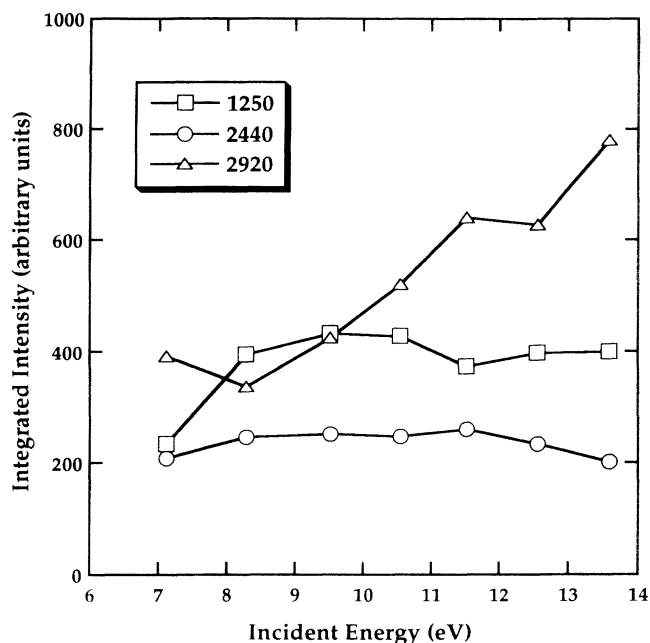


FIG. 2. Integrated intensities of three loss features in HREEL spectra of H/C(100) as a function of incident energy. Intensities were normalized to the background as described in the text.

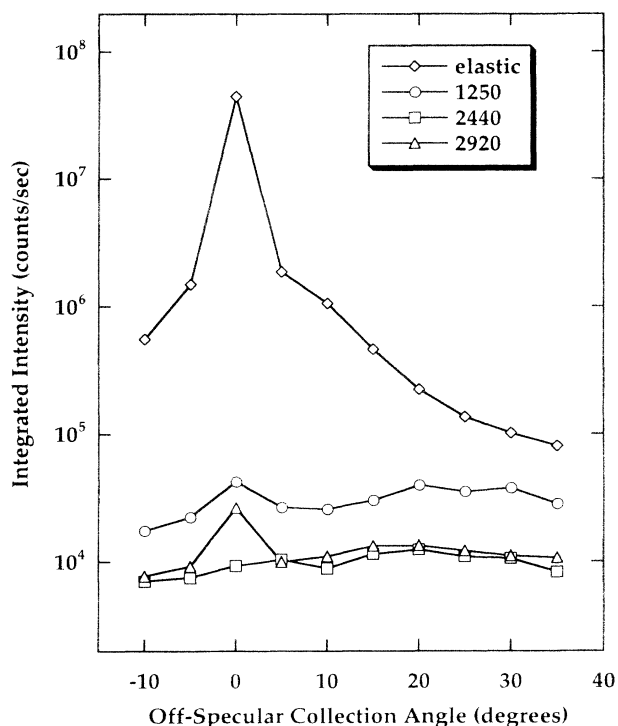


FIG. 4. Angular dependence of spectral features from H/C(100) surface *B* as explained in the text. Shown are absolute integrated HREELS intensities as a function of collection angle.

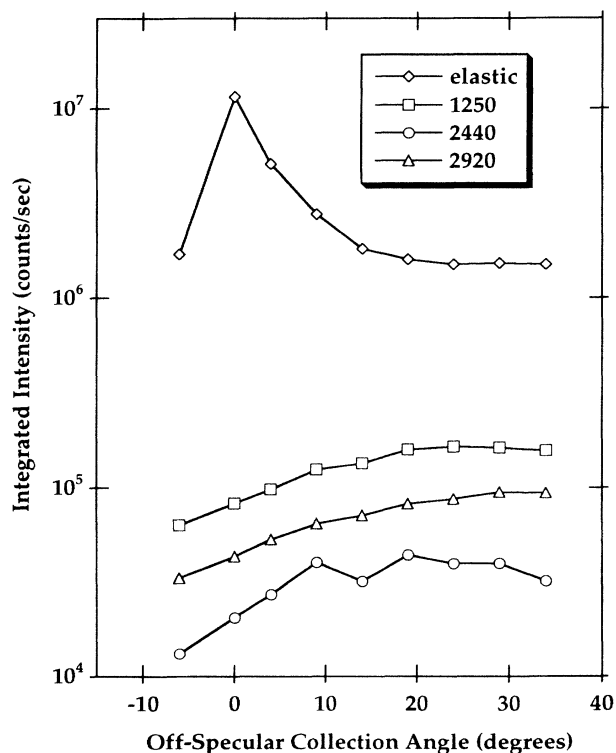


FIG. 3. Angular dependence of spectral features from H/C(100) surface *A* as explained in the text. Shown are absolute integrated HREELS intensities as a function of collection angle.

sities as a function of collection angle from the specular direction for surface *A*. The sample orientation was such that the analyzer rotated approximately along a $\langle 001 \rangle$ azimuth and increasing collection angle indicates electrons scattered more toward the surface normal. The elastic-peak intensity exhibits a decrease with increasing angle off the specular direction. A total decrease of about an order of magnitude is observed over a nearly 40° change in collection angle. In contrast, the intensities of the loss features exhibit a small increase as the collection angle is increased, appearing to peak near 25° off specular.

Figure 4 shows the integrated intensities as a function of collection angle from the specular direction for surface *B*. Again, the elastic-peak intensity exhibits a decrease with increasing angle off the specular direction; however, in this case a decrease of about 3 orders of magnitude is observed. In addition, the intensities of the loss modes at 1250 and 2920 cm^{-1} increase near the specular direction by approximately a factor of 2. No peaking near the specular direction is observed for the intensity of the loss peak at 2440 cm^{-1} . Neglecting the increase near the specular direction, the loss intensities again show a general increase with increasing collection angle, possibly reaching a maximum 20° to 25° off specular.

DISCUSSION

Previous authors have assumed dipole selection rules to be valid for HREELS spectra acquired in the specular

direction from hydrogen-terminated diamond surfaces.^{12,15} However, the relative intensities of vibrational peaks measured in this paper are inconsistent with dipole-scattering selection rules. The peak assigned to CH bending vibrations is observed, in this work and in all other HREELS of hydrogen-terminated diamond surfaces, to be more intense than all other modes including the CH stretching vibration.⁹⁻¹⁷ This is surprising at first glance, since the CH bend should be forbidden by the dipole selection rule for CH bonds oriented normal to the surface. Ideal hydrogen termination of C(111) would produce CH bonds normal to the surface, while the monohydride dimer-row reconstruction of hydrogenated C(100) contains CH bonds only about 20° from the surface normal.²¹ A similar trend has been observed in the intensities of SiH vibrations on various Si surfaces and has recently been attributed to the dominance of impact scattering.²² It has already been pointed out that impact scattering would be expected to dominate on polycrystalline surfaces due to the orientational averaging produced by surface roughness.²³ However, the role of impact and dipole scattering as well as resonant processes on smooth, single-crystal diamond surfaces must be determined before HREELS spectra can be correctly and confidently interpreted.

One possibility for the vibrational-excitation mechanism of low-energy electrons scattered from diamond surfaces is a resonant process involving the formation of a temporary negative ion. The decay of this negative ion often results in the emission of an electron possessing less translational energy than the incident electron. This energy loss is due to a vibrational excitation of the surface and produces a HREEL spectrum with vibrational-loss features. This mechanism has been observed and studied recently for oxygen physisorbed on graphite.²⁴ Since formation of a negative ion is a resonant process, the cross section will be very energy dependent and this energy dependence will result in a peaked dependence of the intensity of vibrational-energy losses on incident electron energy. As seen from Fig. 2, no resonances are observed in the case of H/C(100) indicating that resonant processes are not a major contribution to the excitation cross section in the incident energy range used in this work. Therefore, we next discuss the roles of dipole- and impact-scattering mechanisms in the vibrational spectra of diamond surfaces.

Dipole and impact scattering can be definitively distinguished by examining the dependence of absolute intensities on collection angle.^{25,26} Dipole scattering causes distributions that are highly peaked about the specular direction, while impact scattering produces a much broader angular distribution often peaked away from the specular direction. As shown in Figs. 3 and 4, we have determined the angular dependence of the loss intensities for two different surface preparations of H/C(100). Both surfaces are fully hydrogen terminated, only the smoothness as determined by the LEED measurements is different. Surface *A* produced LEED spots to energies of 35 eV, while surface *B* showed a pattern at 13 eV.

As seen in Fig. 3, CH vibrational-loss intensities from surface *A* increase toward specular collection, but by less

than a factor of 10, far less than is seen on metal surfaces.²⁵ The angular dependences of the loss features demonstrate that impact scattering dominates the spectrum of vibrational losses from H/C(100) since the loss intensities do not increase near the specular direction. It should be noted that even surface *A* is likely smoother than most diamond surfaces studied in previous work. Previously reported LEED patterns from H/C(100) have been at energies ≥ 50 eV.

Vibrational-loss intensities at 1250 and 2920 cm^{-1} from surface *B*, shown in Fig. 4, are peaked in the specular direction, while the elastic intensity is nearly a factor of 1000 higher in the specular direction than 35° off specular. The additional specularly of the elastic peak confirms the increased smoothness of surface *B*. The increase of the loss intensities in the specular direction indicates that a dipole-scattering mechanism is operative. Only about a factor of 2 increase of these loss intensities in the specular direction is seen. Therefore, even for this extremely smooth surface, the intensity of the loss features at 1250 and 2920 cm^{-1} is not dominated by dipole scattering. About half of the intensity observed in the specular direction for each of those two peaks is due to dipole scattering, while the other half is due to impact scattering. The feature at 2440 cm^{-1} , assigned to an overtone of the 1250- cm^{-1} peak, only exhibits impact scattering.

Why should impact scattering be observed as the operative scattering mechanism on diamond? Ibach and Mills²⁶ derive the following formula for the ratio of intensity contributions from impact to dipole scattering:

$$I_{\text{impact}}/I_{\text{dipole}} \sim (h\nu/Re^*)^2, \quad (1)$$

where $h\nu$ and e^* are, respectively, the energy and the dynamic-dipole moment of the vibration and R is the reflectivity of the surface to low-energy electrons. The relative contribution of impact scattering is therefore enhanced for high-energy, low-dynamic-dipole vibrations on surfaces with low reflectivity. The dynamic dipole of a typical CH stretch vibration is small, approximately $0.05e$, while the dynamic dipole of the CH bend is expected to be far smaller.²⁶ Since dipole scattering appears to dominate in the specular direction on metal surfaces even in the case of small dynamic-dipole vibrations, it appears that low reflectivity is the main reason impact scattering dominates on both silicon and diamond surfaces. Low reflectivity of the diamond surface to low-energy electrons is in agreement with the observations of Lurie and Wilson in low-energy electron-diffraction (LEED) experiments.²⁷ They observed almost completely kinematical scattering, which they attributed to the low scattering factor of carbon. This weak scattering may also explain the ability to observe LEED patterns on polished surfaces known to be rough.⁷

The dominance of impact scattering in HREELS has several implications. First, orientational information about surface vibrations is much harder to obtain than it is on surfaces where one can exploit the dipole selection rule. Although there are selection rules applicable for impact scattering, they are more difficult to use and re-

quire a more detailed knowledge of the surface.²⁶ Second, quantification of HREELS intensities is more difficult. Changes in surface order will change the angular distribution of the elastically scattered electrons without significantly altering the loss intensities. Therefore, HREELS intensities from single-crystal diamond should be normalized to incident electron current or to background intensities and not to peak elastic intensity. In contrast, data collected from polycrystalline samples are effectively averaged over angles larger than the width of the dipole lobe and normalization to elastic intensities is justified. Third, since the loss features have a different angular distribution than the elastic peak, instrumental factors may result in observed energy widths of the losses larger than that of the elastic peak. In other words, the instrumental convolution function is dependent upon the angular distribution of the scattered electrons and peak deconvolution using the elastic peak to determine this function may be inappropriate.

The dominance of impact scattering for H/C(100) observed in these experiments does not imply that this will be the case for all HREEL spectra from all diamond surfaces. Although we believe we have created a very smooth and well-ordered surface based on LEED results, an even smoother surface may have a higher reflectivity and, therefore, would show increased intensity of dipole scattering relative to impact scattering. In addition, other crystal faces, i.e., C(111) or C(110), may have higher or lower reflectivity. Vibrations due to other surface adsorbates may show more dipole activity. In the course of these experiments, we have also observed that a vibrational peak due to oxygen adsorbed on C(100) is peaked in the specular collection angle, even for a surface similar to surface *A*. We see that the vibration due to surface oxygen is more dipole active than the C-H modes, consistent with a higher dynamic-dipole moment for C-O than for C-H modes.

In addition, the observation of dipole scattering is a necessary but not sufficient condition to justify application of the dipole selection rules. Dipole selection rules, suppression of modes with a parallel dynamic-dipole moment, and enhancement of modes with a dynamic dipole normal to the surface, arise from the dielectric response of the substrate. Since diamond possesses a small dielec-

tric constant, the response of the substrate may be insufficient to produce dipole selection rules.

The recent popularity of HREELS to investigate diamond surfaces is due to the surface sensitivity and chemical and bonding site specificity. The conclusion that the collected electrons are in many cases dominated by those that have undergone impact scattering does not lessen these strengths. However, it does imply that the scattering mechanism needs to be verified in any particular case before dipole selection rules are applied. HREELS intensities from diamond can, in some cases, be used quantitatively.²³ With a more complete understanding of the factors necessary for correct data interpretation, HREELS will continue to be a powerful tool for investigating the physics and chemistry of diamond surfaces.

CONCLUSION

Vibrational excitation during scattering of low-energy electrons from hydrogen-terminated C(100) exhibits dipole scattering only for extremely smooth surfaces. For H/C(100), which showed a two-domain 2×1 LEED pattern at an incident energy of 13 eV, approximately half the intensity in loss modes at 1250 and 2920 cm^{-1} in the specular direction was due to dipole scattering. On less smooth surfaces, loss features result almost exclusively from impact scattering. The interpretations of results from all low-energy electron spectroscopies on diamond should be affected by this conclusion. For HREEL spectra from hydrogenated diamond surfaces, dipole-scattering selection rules may not be fully applicable, broadened loss features may result, and orientation information is not easily available from HREEL spectra.

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