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# Photoabsorption and photoemission of magnesium diboride at the Mg K edge

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## Abstract

The Mg K edge photoabsorption spectrum and the B 1s, Mg 1s, Mg 2p and valence band photoemission spectra of polycrystalline magnesium diboride have been measured. The photoabsorption spectra of the diboride and the oxide, which is present as an impurity, were separated by measuring the Auger electron partial yield at electron energies characteristic of each phase. The spectra are consistent with published calculations of the density of unoccupied p symmetry states. Better agreement is obtained with calculations for the ground state of the system than with ones for the excited state. Valence band photoemission spectra were measured at photon energies corresponding to core resonances, but, within the signal to noise level of the spectra, no resonant enhancement was observed. This is consistent with the delocalized nature of the valence band.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Magnesium diboride is a high temperature superconductor [1], which is particularly promising for applications due to its large critical current. It is also a material in which two band superconduction has been shown to exist, via coupling of phonons to the  $\sigma$  and  $\pi$  bands. The crystal structure of MgB<sub>2</sub> is of the AlB<sub>2</sub> type, and consists of hexagonal sheets of boron stacked one above the other, with Mg intercalated.

Discussion continues regarding its electronic structure [2], but it appears to belong to the class of 'classical' superconductors described by BCS theory. The occupied band structure consists mostly of B derived bands, and the magnesium is believed to be substantially ionized [3, 4]. However, Kortus *et al* noted that the very small charge found on the Mg atom was partly the result of choosing a small muffin tin orbital size in the calculation.

Core level photoemission is a powerful method for understanding the electronic structure of materials but so far has not been extensively applied to MgB<sub>2</sub> [5–9]. Part of the reason for this is the limited availability of suitable samples, and their preparation with a clean stoichiometric surface. The cleanliness of the surface assumes great importance at low electron kinetic energies, where the spectra are particularly sensitive to the surface. Furthermore, the most common

method for cleaning surfaces in ultrahigh vacuum, sputtering, may change the stoichiometry of the surface, and influence spectra taken under surface sensitive conditions.

Some Mg 2s, Mg 2p and B 1s photoemission data have been reported [5–8]. Vasquez *et al* [5] reported a value of 49.35 eV for the Mg 2p binding energy, compared with 48.9 and 51.0 eV for MgO and MgF<sub>2</sub>, respectively. The literature value for the 2p<sub>3/2</sub> binding energy of metallic Mg is 49.45 eV [10], with a reported value of 280 meV for the unresolved spin–orbit split doublet [10]. The small binding energy shift of the Mg 2p core level in MgB<sub>2</sub> with respect to the metal along with a lower binding energy than the other magnesium-containing compounds suggests that the Mg is not completely ionized. Goldoni *et al* [6] reported a Mg 2p binding energy of 51.7 eV under surface sensitive conditions (low electron kinetic energy), however this measurement was for an oxidized surface. These authors also used a different preparation method from that used by Vasquez *et al* [5] and furthermore they also reported degradation of the surface under synchrotron radiation. Dobrodev *et al* [9] calculated the Mg 2p core level spectrum of MgB<sub>2</sub> and concluded that strong satellite structure should be present due to charge transfer excitations, with a first peak at 2 eV below the main line. They quoted as yet unpublished work which appeared to show a similar structure. However, this structure was not present in the high

**Table 1.** Binding energies of MgB<sub>2</sub> core levels. Estimated accuracy:  $\pm 0.2$  eV.

Core level	Present result (eV)	Reference [8]	Reference [5]	Mg metal [10]
Mg 2p <sub>3/2</sub>	49.6	—	49.35	2p <sub>3/2</sub> 49.45, 2p <sub>1/2</sub> 49.73
Mg 2s	88.6	88.64	—	88.62
B 1s	186.85	—	186.55	—
Mg 1s	1303.3	—	—	1303.4

resolution Mg 2s spectrum of Petaccia *et al* [8], although admittedly this is a different core level. Nevertheless, the Mg 2s line of the boride was found to be much broader than that of Mg metal. Petaccia *et al* fitted their data with a Doniach–Sunjic line shape, and interpreted the increased width of the spectrum in terms of a higher density of states at the Fermi level than in the metal. In light of the calculations of Dobrodev *et al* [9], an alternative interpretation is that charge transfer excitations occur, which are however unresolved.

Uchiyama *et al* [11] showed from angle resolved valence band photoemission spectra of MgB<sub>2</sub> that degradation of cleaved single crystals occurred as a function of time in vacuum. Angle resolved photoelectron spectra of the valence band have been reviewed recently [12] and related to theoretical band structure calculations.

Theoretical [13] and experimental [14] Mg K edge NEXAFS spectra have been reported, and the latter were measured using electron yield and fluorescence modes. Clearly further investigation of the electronic structure of MgB<sub>2</sub> is important as superconductors are a major area of modern scientific activity, requiring reliable data as basic as the core level spectrum, the valence band electronic spectrum, and the photoabsorption spectrum. In this work we report new results concerning the Mg 1s core level, using photoemission and photoabsorption.

## 2. Experimental details

The samples were spark plasma sintered magnesium boride, produced in vacuum at a uniaxial pressure of 80 MPa, and supplied by Dancer, who has characterized the structural and magnetic properties and the critical temperature of these samples [15]. Pieces of a few mm square were cut with a diamond saw. They were placed in a glove bag under a protective nitrogen atmosphere, scraped with a diamond file to remove surface oxide, and then etched, following the procedure of Vasquez *et al* [5]. They were rinsed in dry ethanol, blown dry with nitrogen and inserted into vacuum within about 2 min. The material contains oxides both in the bulk (estimated by Dancer to be 7–8% from x-ray diffraction, [16]) and on the surface. These impurities cause some experimental difficulties, in particular the spectral signatures of the separate phases need to be separated. In photoemission, separate peaks are observed, and we describe below how we separate the x-ray absorption spectra of the boride and oxide phases. The impurities do not affect the electronic properties of the boride as they are present as a separate phase. The advantage of using these samples and this preparation method is that the material has a structure close to that used in applications.

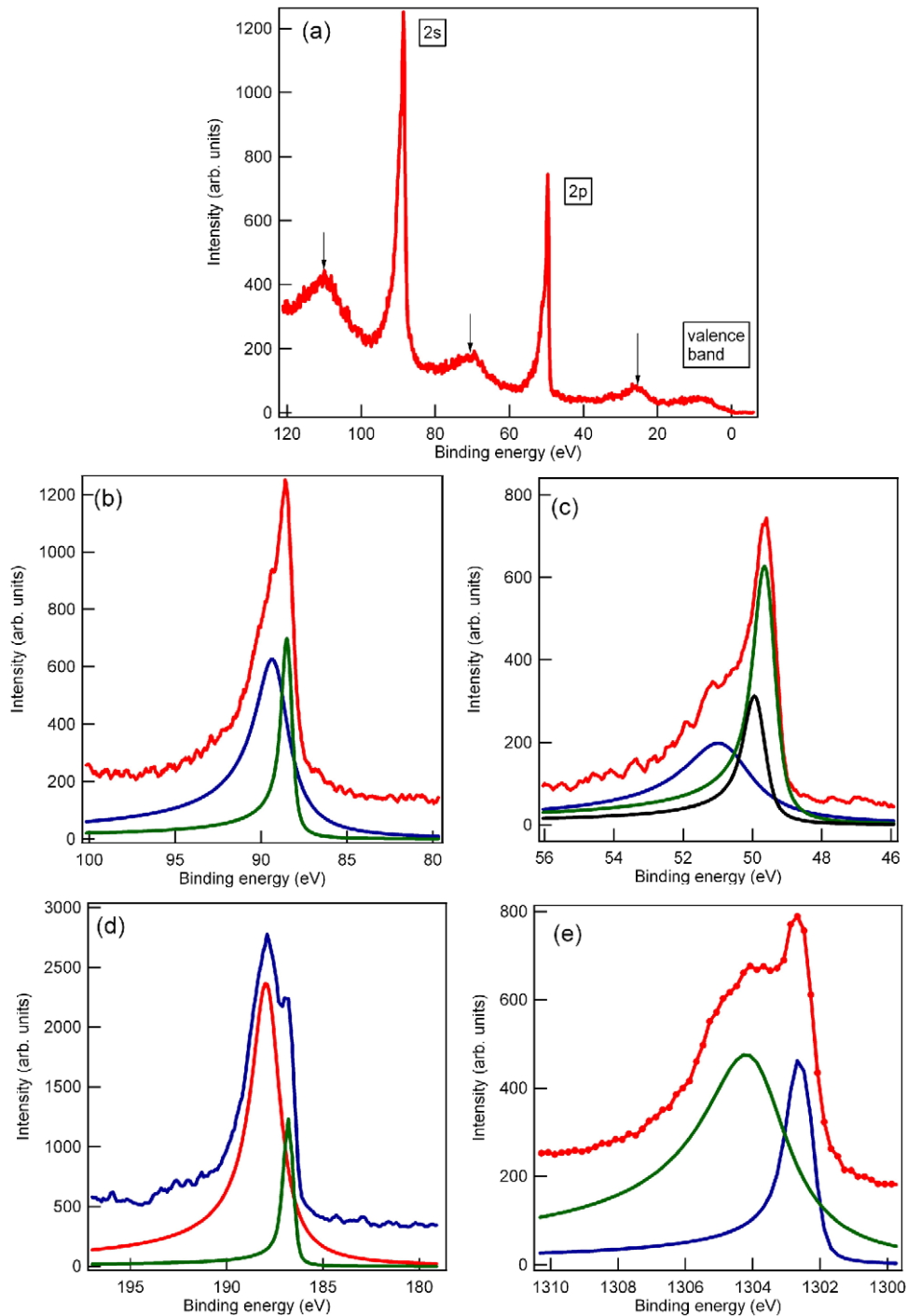
As mentioned above, Uchiyama *et al* [11] as well as other authors have reported changes in the sample spectra due to the effects of synchrotron radiation. We did not observe changes in the present study, and there are two probable reasons. Firstly, previous studies were performed under very surface sensitive conditions, whereas the present study is much more bulk sensitive due to the high kinetic energy of the photons and electrons. Secondly, the preparation procedure does not yield a perfectly clean surface, which is not necessary anyway as the method is bulk sensitive. A partly oxidized surface is likely to be more resistant to further oxidation.

The measurements were performed on the soft x-ray beamline at the Australian Synchrotron [17]. Photoemission spectra were measured with a SPECS Phoibos, 150 mm mean radius electron energy analyser. The resolution of the photons was set to 0.22 eV (1310 eV), 0.26 eV (1495 eV) and 0.41 eV (1996 eV), while the analyser resolution was set to 0.3 eV. The energy scale of the analyser had been previously calibrated using the following metal core levels: Au 4f<sub>7/2</sub> = 84.0 eV, Ag 3d<sub>5/2</sub> = 368.27 eV, Cu 2p<sub>3/2</sub> = 932.67 eV [18]. During the experiment, the Au 4f<sub>7/2</sub> core level was used as a reference and to calibrate the photon energy.

Near edge x-ray absorption fine structure (NEXAFS) spectra were acquired in two modes, firstly by measuring the drain current from the sample, and normalizing to the flux, proportional to the drain current from a mesh intercepting part of the beam. The second method of measuring NEXAFS spectra was by partial Auger electron yield. These spectra were acquired by measuring KLL Auger spectra at a series of energies, and integrating the signal over selected electron energies, as described below.

## 3. Results

The Mg 2s, Mg 2p, B 1s and valence band photoemission spectra at a photon energy of 1495 eV, together with the Mg 1s spectrum at 1996 eV, are shown in figure 1, and the energies summarized in table 1 along with literature values. At 1495 eV the kinetic energy of the Mg 1s photoelectrons is about 192 eV and thus very surface sensitive. As a result only surface contamination was observed at this photon energy (spectra not shown), and hence the results presented here are for a photon energy of 1996 eV, where the kinetic energy is about 693 eV. At a photon energy of 1495 eV, the kinetic energies of the Mg 2s, Mg 2p and B 1s core level electrons are sufficiently high to be bulk sensitive, and the signal is higher due to higher flux and cross-section. These levels were therefore measured at 1495 eV, while at 1996 eV, both the Mg 1s and 2p core levels were measured, with the latter forming a link between the two measurements.

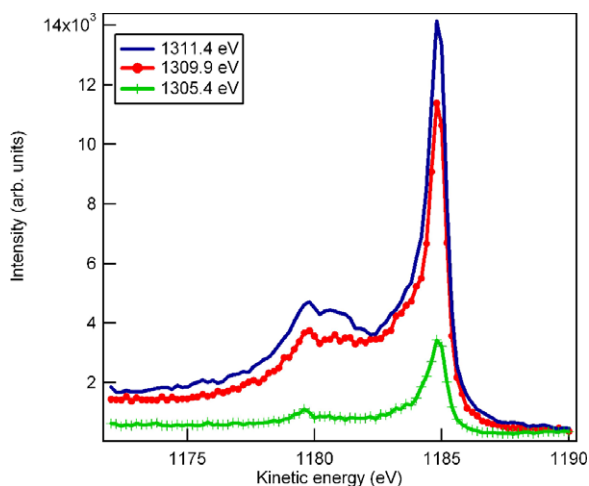


**Figure 1.** (a) Broad scan spectrum of the Mg 2s, 2p core levels and valence band. The arrows mark plasmon losses. Photon energy 1495 eV. (b) Mg 2s core level spectrum (upper curve), with fitted boride (lower right) and oxide (lower left) curves. Photon energy 1495 eV. (c) Mg 2p core level spectrum, with fitted  $2p_{1/2}$  and  $2p_{3/2}$  boride (right) and oxide (left) curves. Photon energy 1495 eV. (d) B 1s core level spectrum, with fitted boride (lower right) and oxide (lower left) curves. Photon energy 1495 eV. (e) Mg 1s core level spectrum (upper curve), with fitted boride (lower right) and oxide (lower left) curves. Photon energy 1996 eV.

At these high photon energies, the Fermi level of the valence band is poorly defined and absolute binding energies were referenced to the Au  $4f_{7/2}$  core level, measured on a piece of Au foil. Since this involves measurement on a different part of the sample holder, the absolute accuracy of the energy is slightly lower than the relative energy of two core levels measured at the same photon energy. The valence states of the

boride are composed predominantly of B 2p states which have a much lower cross-section at high energy than O 2p derived states, so the valence band is dominated by impurities.

The Mg 1s core level was fitted with a convolution of a Doniach–Sunjić line shape for the boride phase (which is metallic) and a Gaussian function to model experimental resolution and non-lifetime broadening (such as phonon



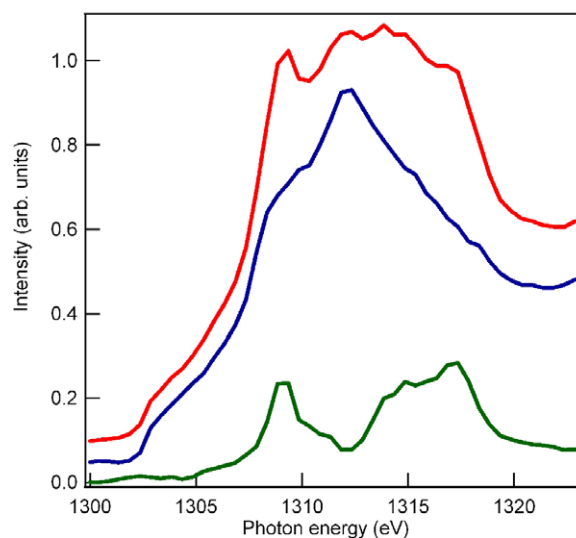
**Figure 2.** KLL Auger spectra of  $\text{MgB}_2$  at energies (bottom to top): 1305.4, 1309.9 and 1311.4 eV, respectively.

broadening). The oxide phase peak was also modelled with a Doniach–Sunjić line shape and a much broader Gaussian function. The 2s and 2p core levels were fitted similarly, with a pair of spin–orbit split peaks for the 2p core levels, which however were not resolved experimentally.

The resulting binding energies are in good agreement with the value of Petaccia *et al* for the Mg 2s level [8]. There is fair agreement with the values of Vasquez *et al* for the Mg 2p and B 1s level, as our values are systematically 0.3 eV higher, but this is within the estimated absolute errors.

As stated above, NEXAFS spectra were measured both by means of drain current from the sample and by Auger electron yield. The drain current yields a spectrum that is bulk sensitive, with a probing depth of the order of several nm. The signal is due to all phases containing Mg, i.e.  $\text{MgB}_2$ , bulk oxide impurities and surface contaminants. The surface sensitivity of the Auger electron yield spectrum is determined by the kinetic energy of the Auger electrons, which is about 1180 eV. At this energy the spectrum is relatively bulk sensitive, but probably less so than the drain current spectrum. Examples of Auger spectra just above the threshold of 1303.3 eV are shown in figure 2. The peak at 1184.8 eV is due to the  $\text{MgB}_2$  phase, while that at about 1180 eV is mainly due to oxide and possibly other impurity phases, such as surface hydroxide or carbonate [5]. The Auger electrons from impurities have lower kinetic energy, firstly because the K and L core levels have higher binding energy, and secondly because the impurities are insulators and have substantial bandgaps.

By integrating the electron intensity around 1185 eV, and plotting it as a function of photon energy, the partial Auger yield NEXAFS spectrum of the boride phase was obtained. This is shown in figure 3, together with the drain current spectrum, which is proportional to the sum of the boride and impurity spectra. Thus if the spectra are suitably normalized and subtracted, the resulting spectrum is the impurity spectrum. Constant backgrounds have been subtracted from both spectra. The two spectra were normalized to unity and then the boride phase spectrum (multiplied by a factor less than one)



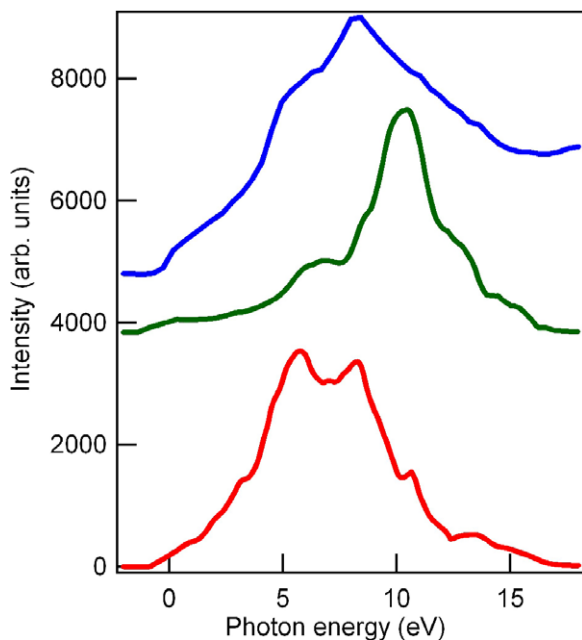
**Figure 3.** NEXAFS spectra of  $\text{MgB}_2$ . Upper curve: spectrum derived from drain current of sample. Middle curve: Auger yield spectrum (kinetic energy  $1185.4 \pm 0.8$  eV). Bottom curve: weighted difference of normalized spectra.

subtracted, to yield the spectrum of the impurities, bottom curve.

Integration of the intensities in the region of the oxide KLL Auger peak and plotting against photon energy yielded a spectrum (not shown) which was a mixture of the boride and impurity spectra. The reasons for this are that there may be a contribution to the signal from the boride phase, and secondary electrons created after photoabsorption by the boride phase underlie this peak, and thus contribute to the signal in this region. For this reason, a more reliable impurity spectrum is obtained by subtracting the weighted boride partial yield spectrum from the total yield (drain current) spectrum.

The onset of the boride NEXAFS spectrum in figure 3 is observed at  $1302.6 \pm 0.5$  eV, and the measured 1s binding energy is  $1303.3 \pm 0.2$  eV. These numbers should be equal for a metallic sample, and in fact the extremes of the error bars do overlap, which is fair agreement. The larger errors for NEXAFS are due to the fact that the monochromator is an optomechanical system which must be scanned for a spectrum, and mechanical errors are larger than in photoemission. In photoemission the calibration is carried out by measuring the sample and a gold standard sample without changing the monochromator setting, and accuracy depends mainly on the stability of the analyser electronics.

The impurity spectrum in figure 3 can be compared to the spectra of Hsieh *et al* [14]. Our impurity spectrum matches their MgO spectrum quite well, suggesting that our Mg-containing impurities are either oxide, or phases with NEXAFS spectra similar to the oxide. The overall shape of the magnesium boride spectrum agrees with their sample S4, which appears to be their purest sample. They reported an onset at energy 1304 eV, compared with our value of  $1302.6 \pm 0.5$  eV. However, Hsieh *et al* calibrated their energy scale to the inflection point of a Mg metal spectrum at 1303.0 eV, while Bearden [10] gives the Mg 1s binding energy as 1303.4 eV.



**Figure 4.** Comparison of our experimental x-ray absorption spectrum with the theoretical spectra of Leiro *et al* [13]. Top curve: experimental spectrum; middle curve: theoretical spectrum neglecting core hole state; bottom curve: theoretical spectrum including core hole state. Photon energies are plotted with respect to the onset. The theoretical spectra have been broadened by smoothing with a box function of width 1.5 eV.

Taking account of the different calibration the discrepancy between our value and theirs for the onset is larger. The difference between the value measured here and by Hsieh *et al* cannot be due to impurity levels, as x-ray absorption measures a neutral excitation. Thus there can be no charging effects. Furthermore, the onset is the Fermi level, and so there are no effects such as doping which could occur in a semiconductor.

We can also compare our data to the theoretical spectrum of Leiro *et al* [13], who calculated not just the density of states, but took account of the effect of the core hole in the final state. In figure 4 we compare our data with their figure 1, which showed the Mg K edge spectrum for their largest supercell of 24 atoms. This spectrum is compressed with respect to ours: we see the first shoulder at about 6.5–7 eV above threshold, and a peak at 10 eV, whereas their spectrum shows these features at about 4 and 6 eV, respectively. On the other hand, our spectrum is quite close to their calculated spectrum for core excitation with the ground state valence electronic structure (i.e. without including the core hole), with a shoulder at about 6 eV and a peak at about 10 eV, see figure 4, middle curve. This seems to suggest that the effect of the final state core hole is not as strong as has been estimated. This could happen if the screening is stronger than expected and agrees with the results of Hsieh *et al* [14] who also interpreted their spectra in terms of the density of p states.

In light of the calculations of Dobrodev *et al* [9] one possible mechanism for additional screening is by charge transfer, rather than simple polarization of the valence charge. Such a mechanism would also explain the relatively low Mg 1s binding energy. As noted above, some authors consider that

Mg is almost completely ionized, and in this case we would expect the peak to be at a high binding energy compared with Mg metal. However, if higher energy satellites are created, then the spectral sum rules for photoemission [19] imply that the main line will appear at lower energy.

The spectrum can also be compared with the B K edge NEXAFS spectrum of Petaccia *et al* [8]. Both spectra probe transitions to states of p symmetry, projected on either the Mg or B sites. At the B K edge, a metallic onset (Fermi level) was observed (as for Mg) as well as features at 2, 6, 10 and 15 eV above threshold. In the present data we observe structures at about 6.5 and 10 eV, indicating that these features correspond to maxima in the density of states at both the Mg and B sites.

Resonant photoemission was attempted at several photon energies near the absorption spectrum, but no enhancement of intensity in the valence band was observed. This is consistent with the view that the electronic structure is delocalized, as resonant enhancement typically occurs for localized and correlated electronic states.

## 4. Conclusions

Photoemission and photoabsorption spectra have been measured of practical MgB<sub>2</sub> samples. In photoemission the main lines due to the boride phase were resolved from impurity features because they appear as distinct features. In photoabsorption, the Mg K edge spectrum was separated from the impurity phase spectrum by means of partial Auger yield detection. The spectral shape is in agreement with previous measurements, but there is some disagreement about the onset energy. The spectrum agrees better with the calculated spectrum neglecting the core hole than with calculations that take account of the hole. This suggests that screening is strong in this compound.

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