

# Infrared absorption of MgO at high pressures and temperatures: A molecular dynamic study

Gboyega A. Adebayo,<sup>1,2</sup> Yunfeng Liang,<sup>3,4,a)</sup> Caetano R. Miranda,<sup>2,4,b)</sup> and Sandro Scandolo<sup>2,4,c)</sup>

<sup>1</sup>Department of Physics, University of Agriculture, PMB 2240, Abeokuta, Nigeria

<sup>2</sup>The Abdus Salam International Centre for Theoretical Physics, Strada Costiera 11, I-34014 Trieste, Italy

<sup>3</sup>International School for Advanced Studies (SISSA), Via Beirut 2-4, 34014 Trieste, Italy

<sup>4</sup>CNR-INFN/Democritos, National Simulation Center, 34014 Trieste, Italy

(Received 22 December 2008; accepted 7 April 2009; published online 6 July 2009)

We calculate by molecular dynamics the optical functions of MgO in the far infrared region 100–1000  $\text{cm}^{-1}$ , for pressures up to 40 GPa and temperatures up to 4000 K. An *ab initio* parametrized many-body force field is used to generate the trajectories. Infrared spectra are obtained from the time correlation of the polarization, and from Kramers–Kronig relations. The calculated spectra agree well with experimental data at ambient pressure. We find that the infrared absorption of MgO at CO<sub>2</sub> laser frequencies increases substantially with both pressure and temperature and we argue that this may explain the underestimation, with respect to theoretical calculations, of the high-pressure melting temperature of MgO determined in CO<sub>2</sub> laser-heated diamond-anvil cell experiments. © 2009 American Institute of Physics. [DOI: 10.1063/1.3146902]

## I. INTRODUCTION

MgO is the second most abundant mineral in the lower Earth's mantle and crystallizes in the rocksalt structure throughout the pressure-temperature range of relevance for the Earth. Due to its structural simplicity and geophysical importance, it is crucial to understand and characterize the properties of MgO under extreme conditions of pressure and temperature of relevance for the Earth's mantle. Of particular importance in this context is the study of the optical absorption by lattice modes in MgO at infrared frequencies (wave lengths  $> 10 \mu\text{m}$ , or frequencies  $< 1000 \text{cm}^{-1}$ ), at pressures up to  $\sim 100$  GPa and temperatures up to 4000 K. Infrared absorption is a fundamental ingredient in thermal conduction models of minerals.<sup>1</sup> At high temperatures, where radiative processes can provide a significant contribution to heat transfer, infrared absorption by lattice modes is, together with optical (electronic) absorption, one of the mechanisms that control the amount of radiative transfer. More importantly, infrared absorption by lattice modes can be used to extract phonon lifetimes, which in turn determine the lattice contribution to the heat conductivity.<sup>1</sup>

A detailed knowledge of the temperature dependence of the IR absorption of MgO at high pressure would also be useful in the interpretation of high pressure melting studies with laser-heating diamond-anvil-cell techniques. In order to avoid the use of external laser absorbers, CO<sub>2</sub> lasers are routinely used in such experiments, since their frequency (950  $\text{cm}^{-1}$ ) is absorbed directly by most minerals, contrary to mid-IR lasers such as Nd:YAG or YLF, whose frequencies

are too high to result in significant absorption through lattice modes, and thus require the insertion of a metal absorber close to the sample. A CO<sub>2</sub> laser was used also in the controversial MgO melting experiment by Zerr and Boehler.<sup>2</sup> Melting experiments on MgO at high pressure are important to put constraints on the solidus in the lower mantle, but the melting line determined in Ref. 2 runs at substantially lower temperatures than the one obtained recently from melting experiments on (Mg,Fe)O solid solutions,<sup>3</sup> and lower than all melting curves determined by molecular dynamic calculations,<sup>4–8</sup> raising concerns about the validity of the different approaches to determine melting.<sup>9</sup> The occurrence of a solid-solid transition has been proposed as a possible cause for the discrepancy.<sup>10,11</sup> Evidence for a solid-solid transition in MgO has been reported recently,<sup>12</sup> but at pressures well above the ones considered in the melting experiment. In the experiment of Zerr and Boehler<sup>2</sup> melting was detected “by visual observation of large increases in temperature due to an increase in the absorption of the melt.”<sup>2</sup> However, the possibility that the large temperature increase could be caused by an increase in the absorption of the solid itself was not considered. The absorption spectrum of crystalline MgO at ambient conditions is dominated by a single peak at about 410  $\text{cm}^{-1}$ , corresponding to the zone-center transverse-optical (TO) vibrational mode of the rocksalt structure. Absorption at higher frequencies, such as those of CO<sub>2</sub> lasers (950  $\text{cm}^{-1}$ ), is caused by anharmonic multiphonon processes and must therefore be strongly temperature dependent, as shown in experiments at ambient pressure.<sup>13,14</sup> Because the steady-state temperature of the sample in diamond anvil cell experiments depends on the absorption coefficient, a nonlinear dependence of the absorption coefficient with temperature may lead to an anomalous dependence of the temperature on the intensity of the laser. We will show that in the case of MgO such nonlinearities yield a nonmonotonic de-

<sup>a)</sup>Present address: Department of Physics and Engineering Physics, University of Saskatchewan, Saskatoon, Canada.

<sup>b)</sup>Present address: Department of Civil and Earth Resources Engineering, Kyoto University, 615-8540 Kyoto, Japan.

<sup>c)</sup>Electronic mail: scandolo@ictp.it.

pendence of the sample temperature with the intensity of the laser, which implies that above a threshold intensity, multiple equilibrium values of the temperature are possible for a given laser intensity. Therefore, in addition to the possibility that the large temperature increase could be caused simply by an increase in the absorption of the solid, the possibility also exists that large temporal and spatial temperature inhomogeneities develop within the sample. Both phenomena lead to an erroneous determination of the melting temperature.

Measurements of the infrared properties of MgO at the conditions of the Earth's mantle are problematic,<sup>15</sup> so a fundamental step toward an improved understanding of the above phenomena consists in the theoretical determination of the infrared absorption spectra of MgO at high pressures and temperatures. The temperature dependence of the infrared spectrum at ambient pressure has been measured in Refs. 13 and 14 and shows substantial temperature induced changes both in the shape and peak positions. The pressure dependence has not been studied in much detail. Inelastic x-ray scattering experiments<sup>16</sup> and *ab initio* phonon calculations<sup>17,18</sup> indicate a strong pressure dependence of the harmonic zone-center frequencies with pressure, with the TO mode reaching a frequency of 560 cm<sup>-1</sup> at 35 GPa. At this pressure the frequency of the LO mode, below which absorption is non-negligible, is calculated to be around 830 cm<sup>-1</sup>. The approaching of the fundamental absorption frequencies of MgO to the CO<sub>2</sub> laser frequency of 950 cm<sup>-1</sup> is an indication that pressure effects lead to enhanced absorption by the laser. A simple extrapolation to 100 GPa yields a frequency of ~1000 cm<sup>-1</sup> for the LO mode,<sup>18</sup> which implies an increase in the absorption by the CO<sub>2</sub> laser light by orders of magnitude with respect to ambient conditions.<sup>2</sup>

In this work we use molecular dynamics to calculate the absorption coefficient and other optical functions for MgO at high temperature and pressure. Optical functions are determined from the frequency dependence of the optical susceptibility by means of Kramers–Kronig (KK) relations.<sup>18</sup> The layout of our work is as follows: in Sec. II we describe the methods, including the KK relations. In Sec. III we present the results and in Sec. IV we discuss the implications of our results on the reliability of CO<sub>2</sub> laser-heating experiments.

## II. METHODOLOGY

Simulations were performed using an *ab initio* parametrized polarizable many body potential,<sup>19</sup> which includes nonspherical distortions of the electronic shell.<sup>20</sup> Such a model reproduces extremely well a number of structural and dynamical properties of solid MgO, including its phonon spectrum.<sup>19</sup> A similar but simpler model<sup>21</sup> has been shown to be able to reproduce the IR spectra of solid SiO<sub>2</sub>, both in the low temperature and high temperature phases.<sup>22</sup> Because the potential used here for MgO contains an improved description of the ions' deformation, we trust the present results are at least as accurate as those presented in Refs. 22 and 23.

In all simulations, 512 atoms of MgO were placed in a simulation cell consisting of 4 × 4 × 4 periclase (rocksalt) conventional cubic unit cells. Each simulation consisted of

three sequential runs, the first consisting in a pressure equilibration carried out in the isothermal-isobaric ensemble (NPT), followed by a temperature equilibration in the canonical ensemble (NVT), and finally by a production run in which the infrared spectrum was obtained in the microcanonical ensemble (NVE). The equations of motion were integrated with the Verlet algorithm and a Nosé thermostat was used to control temperature;<sup>24</sup> each run consisted of 20 ps or longer. Several simulation runs were carried out in the pressure range between 0 and 40 GPa starting from room temperature up to 4000 K.

By Fourier transforming the total polarization autocorrelation function, we are able to calculate the imaginary part  $\varepsilon_2(\omega)$  of the frequency-dependent dielectric function in the classical limit,<sup>22,25</sup>

$$\varepsilon_2(\omega) = \frac{2\pi\omega}{3VK_B T} \int_0^\infty \langle \vec{M}(t) \times \vec{M}(0) \rangle e^{-i\omega t} dt, \quad (1)$$

where  $\vec{M}$  is the total dipole moment,  $V$  is the volume of the sample, and  $K_B$  is Boltzmann's constant, respectively. The complex refractive index  $\tilde{n}$  and the complex dielectric function  $\tilde{\varepsilon}$  are defined as:

$$\tilde{n}(\omega) = n(\omega) + ik(\omega), \quad \tilde{\varepsilon}(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) = \tilde{n}(\omega)^2, \quad (2)$$

which implies

$$\varepsilon_1(\omega) = n(\omega)^2 - k(\omega)^2, \quad \varepsilon_2(\omega) = 2n(\omega)k(\omega). \quad (3)$$

From the calculated  $\varepsilon_2(\omega)$  we obtain the real part  $\varepsilon_1(\omega)$  through the KK relation,<sup>26</sup>

$$\varepsilon_1(\omega) = \frac{2}{\pi} P \int_0^\infty \frac{\omega' \varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega' + \varepsilon_\infty, \quad (4)$$

where  $\varepsilon_\infty$  is the high-frequency electronic contribution to the dielectric function. The value of  $\varepsilon_\infty$  was fixed to 3.01, the experimental value at ambient conditions. Experiments at high temperature<sup>13</sup> and calculations at high pressure<sup>17</sup> show that  $\varepsilon_\infty$  has a negligible dependence on temperature and pressure. The infrared absorption spectrum  $\alpha(\omega)$  can be obtained as  $\alpha(\omega) = \omega \varepsilon_2(\omega) / cn(\omega)$ , where  $c$  is the speed of light, and the reflectivity  $R$  is obtained as

$$R(\omega) = \frac{(n(\omega) - 1)^2 + k(\omega)^2}{(n(\omega) + 1)^2 + k(\omega)^2}. \quad (5)$$

## III. RESULTS

Our results for the relevant optical functions at ambient conditions are compared in Fig. 1 with the experimental results of Hofmeister *et al.*<sup>14</sup> Both experiment and theory use KK relations, but optical functions are derived from the reflectivity in experiments and from  $\varepsilon_2$  in the calculations. The calculated position of the TO peak [Fig. 1(a)] is in good agreement with experiments, although the experimental peak has a slightly larger width. As a result, the static value of the real part of the dielectric function,  $\varepsilon_1(0)$ , which through KK Eq. (4) is related to the integral of  $\varepsilon_2$ , is underestimated by 5% in our results. In Fig. 1(b) we show absorption coefficient

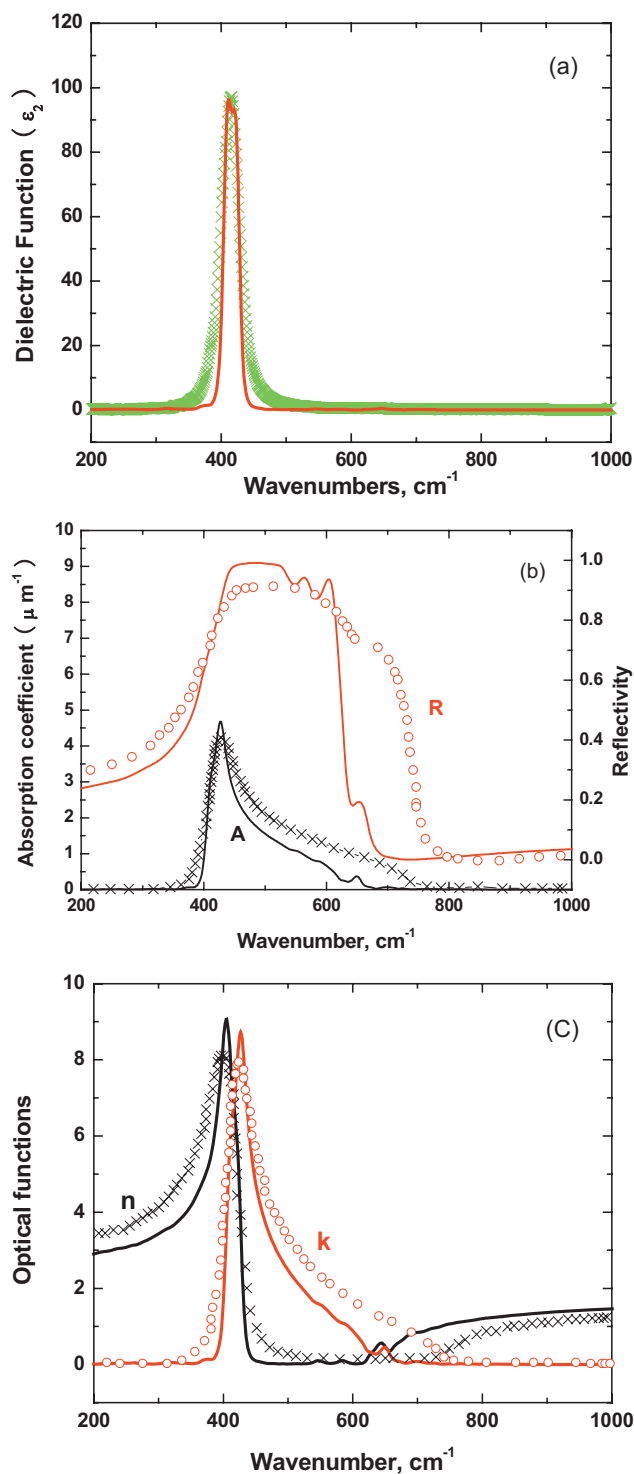


FIG. 1. Calculated optical functions of MgO at ambient conditions and comparison with experimental data. Solid lines are simulation results; symbols are from experiments (Ref. 14).

cients and reflectivity spectra. The overall agreement is good, although the right shoulders of absorption and reflection reduce to zero earlier than experiments. This is consistent with the underestimate of  $\epsilon_1(0)$ . In fact, the high-frequency shoulder vanishes in correspondence to the LO optical mode, and the position of this mode is related to the position of the TO mode by the Lyddane–Sachs–Teller expression  $\omega_{\text{TO}}^2/\omega_{\text{LO}}^2 = \epsilon_\infty/\epsilon_1(0)$ . So an underestimation of  $\epsilon_1(0)$  leads to an underestimation of  $\omega_{\text{LO}}$ . A similar agreement between experi-

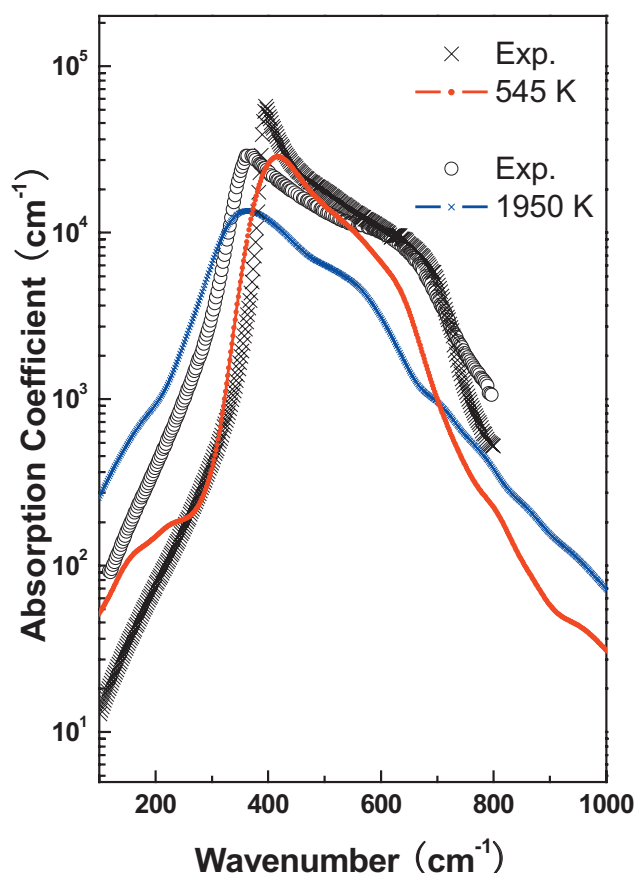


FIG. 2. Calculated absorption coefficients of MgO at 545 and 1950 K and ambient pressure, as compared with the experimental results of Jasperse *et al.* (Ref. 13).

ment and theory is found in optical function in Fig. 1(c); the calculated static refractive index has been underestimated and the gap between low and high frequency band is smaller than experiments. All discrepancies between theory and experiment can thus be attributed to the smaller theoretical value of  $\epsilon_1(0)$ , or, equivalently, to the smaller theoretical value of the effective charge of the TO mode, a likely consequence of the approximate nature of the induced charge deformation in the many-body potential.

Figure 2 shows our calculated absorption coefficients at ambient pressure and 545 and 1950 K, and their comparison with experiments.<sup>13</sup> Again, there seems to be good agreement between theory and experiment as far as the position of the prominent shoulder around 650  $\text{cm}^{-1}$  is concerned, although the height of the peak is underestimated by theory by a factor of about 1/2. In order to highlight the role of temperature in the absorption spectra, we show in Fig. 3 the ratio between the absorption coefficient at 1950 and 545 K. It is interesting to remark that experimental and theoretical curves agree rather better in the low frequency wing (although with a rigid shift), and in the high frequency wing of the spectrum ( $\omega > 700 \text{ cm}^{-1}$ ).

Figure 4 finally shows the results obtained at high pressure (20 and 40 GPa). No experimental data are available at high pressure. Pressure causes the absorption peak to move to higher frequencies, but leaves the shape of the spectrum relatively unaltered. On the other hand, temperature causes a

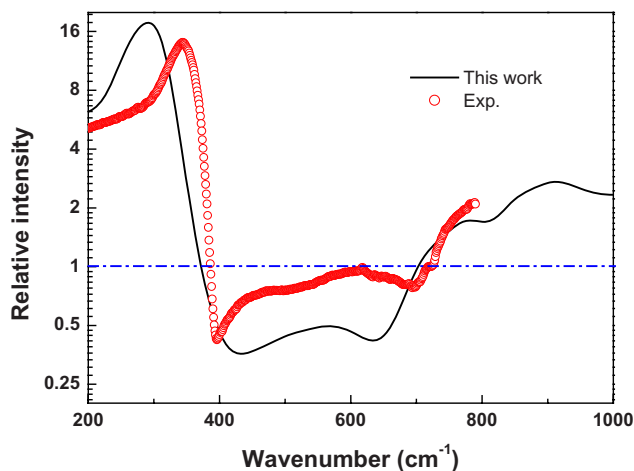


FIG. 3. Ratio between the absorption coefficients at 1950 and 545 K, at ambient pressure. Solid lines are simulation results; symbols are from experiments (Ref. 13).

downward shift of the peaks, and a large increase in the absorption in the wings of the spectra. Within the errors of the calculated data, we found an increase in the absolute value of the absorption coefficient of about three times at frequencies around  $950\text{ cm}^{-1}$ , when temperature is increased from 300 to 3000 K, both at 20 and 40 GPa.

#### IV. DISCUSSION

With the calculated values of the absorption coefficient at high pressure and temperature, we are now in a position to discuss the implications that a temperature-induced increase in the absorption may have on experiments carried by heating MgO samples at high pressure with a  $\text{CO}_2$  laser.

First, the large increase in absorption attributed to the appearance of the melt in the experiment<sup>2</sup> might have been instead caused by an increased absorption within the solid phase. The abruptness of the absorption changes with laser intensity reported in Ref. 2 suggests however a different mechanism, based on discontinuous jumps of the temperature in the sample. For a MgO sample of thickness  $l$  and a laser spot area  $S$ , the rate of heating per unit area, due to the  $\text{CO}_2$  laser can be estimated as<sup>27</sup>

$$R \approx \frac{p_a \alpha(\omega_0) l}{S}, \quad (6)$$

where  $p_a$  is the laser power and  $\omega_0$  is the frequency ( $\sim 950\text{ cm}^{-1}$ ) of the  $\text{CO}_2$  laser. In stationary conditions the heat deposited by the laser will be dissipated through thermal conduction at a rate given approximately by

$$R \approx \frac{\lambda T}{l}, \quad (7)$$

where  $\lambda$  is an average thermal conductivity of the sample or of whatever material separates the sample from the region at ambient temperature, and  $T$  is assumed to be much larger than room temperature. The equilibrium temperature of the sample can be obtained by equating the two expressions. With a reasonable choice of  $l=10\text{ }\mu\text{m}$  and  $S=10^4\text{ }\mu\text{m}^2$ , and the thermal conductivity for MgO taken from Cohen<sup>28</sup> (assuming thus that MgO is in direct contact with the diamond anvil and that the lattice contribution to the thermal conductivity dominates) and the calculated values of  $\alpha$  at 20 GPa, we obtain that in order to reach a temperature of 1000 K, a power of 100 W would be required, while in order to reach 3000 K, a power of 50 W is required. The crudeness of the model implies that the results should be considered as qualitative trends, more than as quantitative estimates. However the qualitative and unexpected result is that, at high temperature, a lower power is required to bring the sample to even higher temperatures, a consequence of the fact that absorption grows faster, with temperature, than the ability of the sample to dissipate the absorbed heat. Because at low temperatures the temperature grows with the laser power, the dependence of the temperature of the sample on the laser intensity is overall nonmonotonic. As a consequence, more than one value of the temperature becomes possible for the same laser intensity, at high temperatures. Such a nonlinear behavior may lead to discontinuous jumps and large fluctuations of the sample temperature either in time or in space, and therefore to an incorrect determination of the melting temperature.

#### V. CONCLUSIONS

We determined the infrared spectra of MgO up to a pressure of 40 GPa and up to 4000 K from molecular dynamics simulations with a polarizable potential, and from KK relations. Calculated spectra agree well with available experiments at ambient pressure. At high pressures no experimental data are available. We find that pressure shifts the absorption peak to higher frequencies, and temperature leads to an increase in the absorption in the tails of the spectrum, due to multiphonon processes. Based on the temperature dependence of the absorption spectra we argue that MgO melting-line determinations in experiments where the sample is directly heated by an infrared laser need to be revisited. In particular, we find that the sample temperature may depend nonmonotonically on the laser intensity, and that multiple values of the temperature are possible for a given laser intensity, at high temperature. As a consequence, the inference that large increases in temperature due to an increase in the

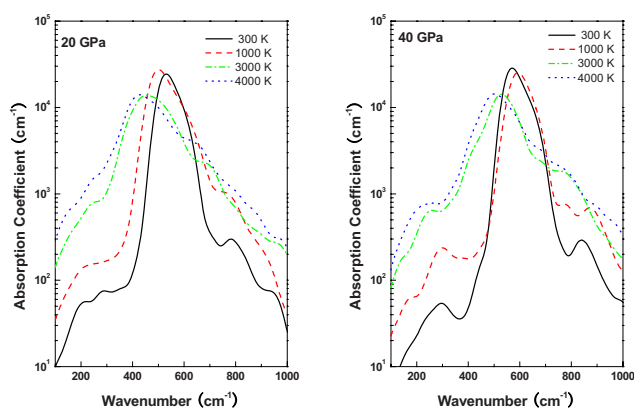


FIG. 4. Calculated absorption coefficient at 20 GPa (a) and 40 GPa (b) at different temperatures.

absorption of the sample are a proof of melting<sup>2</sup> is not necessarily correct. Large increases in temperature are also compatible with the persistence of the solid in the sample, or with melting at much higher sample temperature than predicted based on a smooth extrapolation of the temperature on the laser intensity.

## ACKNOWLEDGMENTS

We would like to acknowledge the financial support of the Italian National Research Council (CNR/INFM) through the European Science Foundation program “EuroMinSci.”

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