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Ellipsometric study of the charge-transfer excitation in single-crystal La_2CuO_4

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The dielectric response functions parallel and perpendicular to the c axis of single-crystal La_2CuO_4 are determined at room temperature from 0.7 to 4.9 eV by analysis of ellipsometric data. Strong anisotropy is observed; for $\mathbf{E}\|c$ the optical properties are nearly featureless in this energy range, while for $\mathbf{E}\perp c$ there is a sharp peak in Im(ε) near 2 eV associated with the O(2p) to Cu(3d) charge-transfer excitation. Additional features are observed on the high-energy side of this peak, and the origin of these is discussed in the light of recent theoretical predictions.

I. INTRODUCTION

The cuprate-based high-T_c superconductors exhibit strongly anisotropic behavior as a consequence of their layered crystal structures. The common feature of all these materials is the presence of Cu-O_2 layers, which form the a-b planes and have short Cu-O bond lengths. These layers are linked together in the c direction with much weaker bonds. The prototypical compound for this class of materials is lanthanum cuprate (La_2CuO_4), which becomes superconducting below ~40 K when the La is replaced with 7–10% Sr or Ba. Since this compound was the first cuprate superconductor discovered and it has one of the simplest crystal structures, it has been the subject of many detailed optical studies. Infrared,[1–4] Raman,[5–9] and transmission[10] or reflectivity[2,11,12] measurements in the visible have shown that La_2CuO_4 appears more like an insulator when the optical electric field is perpendicular to the Cu-O_2 planes and more like a conductor when it lies in these planes. The visible optical studies are particularly important in these materials since they yield direct information about the electronic states near the Fermi level, which are ultimately the states involved in superconductivity. In addition, through correlations with resonance Raman data,[13] they yield information about the electron-phonon interactions, which are a central ingredient in the BCS theory of superconductivity.

In this paper we determine the anisotropic optical properties of La_2CuO_4 in the range 0.7–4.9 eV based on analyses of ellipsometric data from an oriented single crystal. These are the first such measurements to our knowledge on oriented crystals of this material, and they are likely to be more reliable than the previous determinations of the optical properties based on Kramers-Krönig analyses of reflectivity data.[14] The primary feature in our spectra is a peak in Im(ε) near 2 eV that occurs only for $\mathbf{E}\perp$c. This peak has been attributed to a charge-transfer (CT) excitation from O(2p) to Cu(3d) crystal-field-like orbitals and is a recurrent feature of the insulating precursor phases of all cuprate superconductors.[15–17] The occurrence of this transition is consistent with the conclusion that these materials are charge-transfer insulators with a Mott-Hubbard correlation gap.[18,19]

Falck *et al.*[12] have shown that their measured line shape and temperature dependence of the CT peak in La_2CuO_4 can be fit with a model involving short-range electron-hole interactions in the final state of the CT excitation broadened by coupling to optical phonons. Lorenzana and Yu[20] have developed a more basic theory for the optical conductivity in the vicinity of the CT excitation that agrees with the main features of the experiments.[11,12] This theory predicts considerable structure above the onset of the CT transition, a prediction that has yet to be confirmed. Perkins *et al.*[10] have recently observed at 10 K a narrow absorbance peak in La_2CuO_4 near 0.4 eV that has significant structure on the high-energy side. They attribute this peak to an exciton and suggest that the additional structure is due to multiple magnon excitations. We observe broad features on the high-energy side of the 2-eV CT feature that are qualitatively similar to those seen by Perkins *et al.*[10] for the 0.4-eV exciton and to those predicted by Lorenzana and Yu[20] for the CT excitation. The origin of this structure remains to be determined, however.

There have been previous ellipsometric studies of high-T_c materials, both ceramics[16,21] and single crystals,[17] but none that have successfully determined the two independent dielectric functions. Most high-T_c cuprate materials tend to grow as thin platelets with the c axis normal to the large facets. Such crystals are ideal for determining the dielectric constants ⊥c from Kramers-Krönig analyses of normal incidence reflectivity. However, with ellipsometry one generally needs a large crystal surface containing the c axis, and the data must be obtained for the c axis parallel and perpendicular to the plane of incidence in order to accurately determine both dielectric functions. Lanthanum cuprate is one of the few high-T_c cuprate materials that have been grown with large c-axis surfaces.

II. EXPERIMENTAL DETAILS

The La_2CuO_4 crystal used for this study was grown at the University of Oxford from a CuO flux by spontaneous

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nucleation, as described by Chen *et al.*,[22] and is one of the crystals used in a previous Raman study.[5] The stoichiometry of the crystal is not known, but we anticipate that it contains a small fraction of oxygen vacancies. At room temperature La_2CuO_4 is orthorhombic, but its structure is only a slight distortion ($\sim 1\%$ difference between a and b) of the tetragonal K_2NiF_4 structure.[23] We will thus treat our sample as a uniaxial tetragonal crystal and use tetragonal coordinates to identify crystallographic orientations. The as-grown sample was potted in epoxy and lapped to expose an arbitrary facet. Laue diffraction patterns were then used to orient the crystal for further lapping, exposing a trapezoidal-shaped (100) face with $\sim$4-mm^2 area. However, small inclusions of Cu_2O and surface imperfections due to pits and cracks limited the useful regions of the crystal to about half of this area.

Immediately prior to acquiring ellipsometric data a fresh optical quality surface finish was obtained by polishing the sample with successively finer grits, finishing with an aqueous solution of 0.05-μm colloidal silica, followed by a thorough rinse in methanol. We were initially concerned about using a solution containing water, which has been reported to adversely affect La_2CuO_4 samples.[2] However, more complete studies have shown the degradation to be caused by hydroxides forming on the surfaces of grain boundaries,[24,25] which would necessarily destroy conductivity in polycrystalline samples, but would have marginal effect on bulk crystals. Moreover, measured degradation times for samples soaked in water are on the order of months.[26] For completeness, we also repeated the measurements after etching the crystal in a 1% Br in methanol solution, as suggested by Falck *et al.*,[12] but this did not alter the spectra.

The raw ellipsometric data were recorded with a variable angle spectroscopic ellipsometer manufactured by the Woollam company. The spectral bandwidth of the incident light is determined by the slit openings and was normally 2.4 nm. However, the slits were widened for the data recorded above 4.6 eV to compensate for the reduced intensity available in this region, thereby increasing the spectral bandwidth to 4.4 nm. In energy units the resolution thus varied from $\sim$0.001 to $\sim$0.1 eV at the low- and high-energy limits of our data, respectively.

The standard optics in the ellipsometer produced a well-collimated beam with a spot size at normal incidence on the sample that was $\sim$2.5 mm in diameter. Therefore, it was necessary to use black tape to mask out the epoxy and the bad portions of the crystal to avoid artifacts. Because of the small useful area and low reflectivity from the crystal, the resulting data were of poor quality. Consequently, we modified the ellipsometer by introducing a 38-mm focal length fused-silica lens before the sample, which reduced the beam spot size to $\sim$300 μm, and a second identical lens after the sample, that focused the divergent reflected beam onto the detector. With the small spot size we could concentrate all the light onto a smooth, defect-free portion of the crystal and the optical throughput of the system was increased more than tenfold. However, the incident beam was no longer collimated, but was spread out in a cone of half angle $\sim 1.5°$. In order to convince ourselves that the error introduced by the spread in angle of incidence was relatively small, we examined data from a Si wafer and a sputtered Pd film with and without the lenses in the beam path. We were unable to discern any differences between the fitted dielectric functions from the two sets of data for either material.

III. RESULTS

The ellipsometric quantities $\tan\psi$ and $\cos\Delta$ were measured from 0.7 to 4.9 eV at four angles of incidence for both orientations of the c axis relative to the plane of incidence. Several regions on the crystal were examined to assess the homogeneity of the crystal, and each location was repeated to verify reproducibility. The raw data are shown in Figs. 1 and 2. Note that the angles of incidence were chosen so that the values for Δ bracket the angle of incidence for which $\Delta = 90°$. This angle, referred to as the principal angle, is normally close to Brewster's angle and corresponds to the angle at which the most reliable optical constants can be extracted from the data.[27]

The ellipsometric parameters ψ and Δ are defined by the ratio of the p- to s-polarized reflection coefficients, $r_p/r_s = \tan\psi e^{i\Delta}$. Reflection coefficients for the different scattering geometries in a tetragonal crystal can be derived from Maxwell's equations and are summarized in Table I of Weber *et al.*[28] For each angle of incidence there are four measured quantities and four unknowns, the real and imaginary parts of ε parallel and perpendicu-

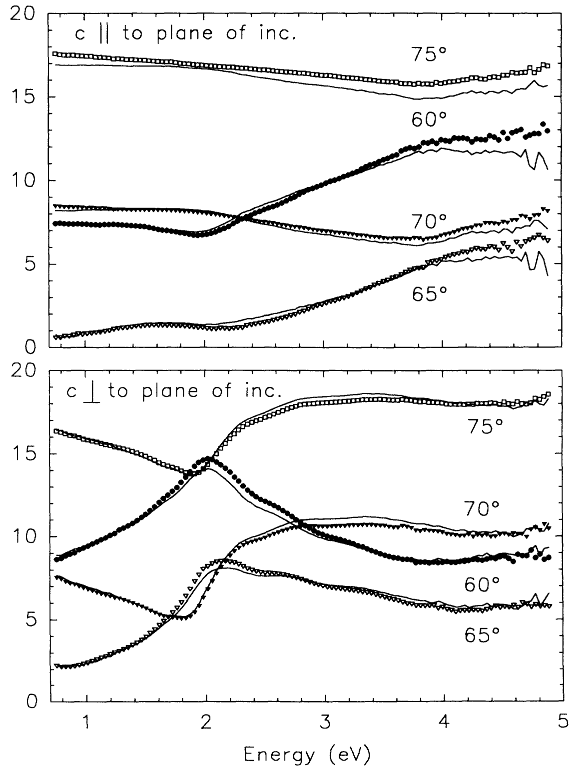

FIG. 1. Measured values of the ellipsometric quantity ψ for the c axis parallel (top) and perpendicular (bottom) to the plane of incidence. The solid lines are calculated values determined from the fitted dielectric functions shown in Fig. 3.

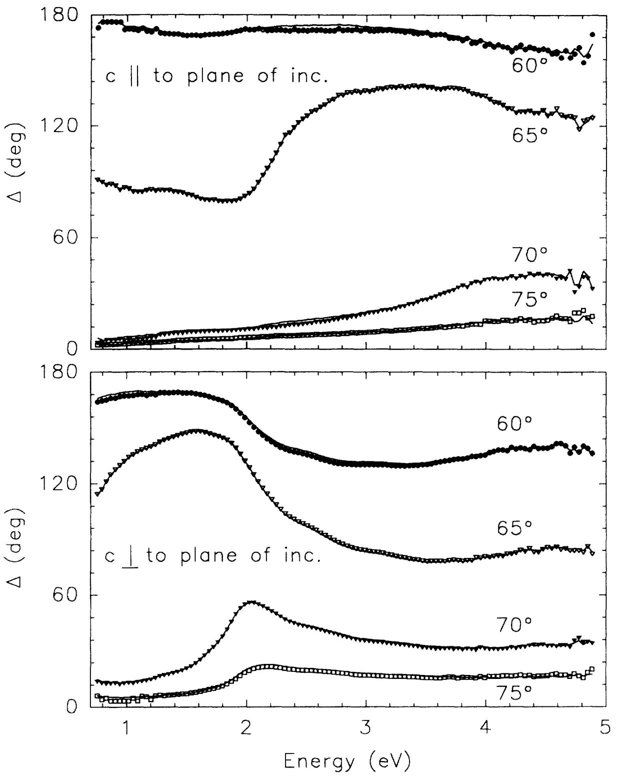

FIG. 2. Measured and calculated Δ values corresponding to the ψ values in Fig. 1.

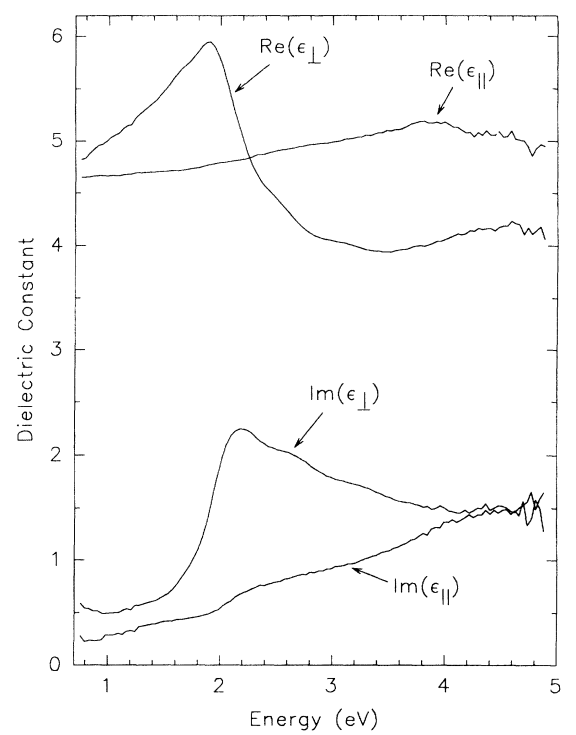

FIG. 3. Dielectric functions for La_2CuO_4 determined from a least-squares fit to the raw ellipsometric data shown in Figs. 1 and 2.

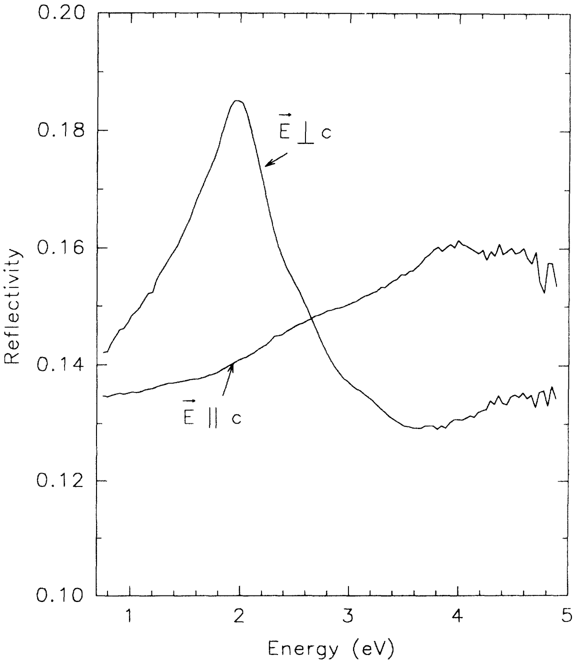

FIG. 4. Normal-incidence reflectivity for the two crystal orientations in La_2CuO_4 calculated from the optical constants in Fig. 3.

lar to the *c* axis. Although it does not appear to be possible to write an explicit expression for the dielectric constants in terms of the measured ellipsometric quantities, the reflection formulas can be solved numerically to obtain a unique solution for the four unknowns. In our case we have measured data at four angles of incidence, and thus have redundant information. Consequently, we used a least-squares-fitting procedure that varied the dielectric constants to minimize the difference between observed and calculated values of ψ and Δ at all four angles of incidence. At each energy 16 data points are fit to determine the four unknowns. The results of the fit are shown in Fig. 3. The solid lines in Figs. 1 and 2 are the ψ and Δ calculated with the fitted values of the dielectric constants. The rms error from the fit to 1792 points is $\pm 0.78°$. However, as can be seen from the figures, the errors are not entirely random. Since the measurements were made at room temperature in ambient conditions, these small systematic errors may be the result of adsorbed layers that are not accounted for in our model. For comparison purposes we also show in Fig. 4 the normal-incidence reflectivity for the two crystal orientations calculated from the optical constants in Fig. 3.

As expected, strong anisotropy is observed. While $\varepsilon_{\parallel}$ is nearly featureless over this energy range, $\varepsilon_{\perp}$ has a strong resonance near 2 eV. Although the structure we observe is qualitatively consistent with previously reported results, there are small differences in the values of the dielectric constants. For example, near 1 eV where there is little structure, our values for $\mathrm{Im}(\varepsilon_{\perp})$ are much larger than those of Uchida *et al.*[11] or Falck *et al.*[12] and much smaller than those of Eklund *et al.*[2] These discrepancies may be caused by problems with the Kramers-Krönig analyses, by errors associated with the angular spread of the ellipsometric data, by variations in the impurity or oxygen vacancy concentrations in the crystals, or by differences in contamination layers or surface roughness.

IV. DISCUSSION

In order to compare our results with the theoretical predictions by Lorenzana and Yu[20] and the observations by Perkins *et al.*[10] we were motivated to fit our data with some simple phenomenological models. Inspection of $\mathrm{Im}(\varepsilon_\perp)$ in Fig. 3 reveals that there are two broad shoulders above the charge-transfer excitation at approximately 2.5 and 3 eV. Therefore, we initially fit the data in the region above 1 eV as a sum of three Lorentz oscillators plus a linear term to account for the nearly isotropic rising background. The results of this 10-parameter least-squares fit are shown in Fig. 5, where the dotted curves are the background and constituent peaks and the thin solid curve at the top is their sum. We identify the strong and narrow peak at 2.11 eV as the primary charge-transfer excitation. The second and third peaks are higher in energy by 0.39 and 1.02 eV, respectively. The predicted spectrum of Lorenzana and Yu[20] is shown at the top of Fig. 5. Here we have converted their optical conductivity to $\mathrm{Im}(\varepsilon)$ and have adjusted their energy scale to match the 2.11-eV peak. The agreement between predicted and observed peak positions and widths is not very convincing.

The peak at 0.39 eV above the CT excitation, however, corresponds closely to that expected for a two-magnon sideband. To demonstrate the correspondence, we show as the bold curve in Fig. 5 a model calculation for this sideband. This calculation involves three steps. First, the two-magnon line shape is calculated using Parkinson's theory,[29] as modified by Weber and Ford,[30] to fit the observed Raman data.[8,31] This line shape, which fits well the Raman spectrum on another La_2CuO_4 crystal from the same batch as the one used here,[30] is then convoluted with the Lorentzian fit to the CT excitation. Finally, the zero of energy is shifted to 2.11 eV. The agreement between this calculated line shape and the second peak in the spectrum is striking; however, we have implicitly assumed that the excited-state exchange interaction constant J' does not differ significantly from its ground-state value, an assumption that is probably not valid. Since there is no theory for the four-magnon line shape, we have simply drawn a vertical arrow in the figure at twice the shift of the two-magnon peak to indicate its approximate position.

Although the experimental line shape for $\mathrm{Im}(\varepsilon_\perp)$ appears consistent with two- and four-magnon sidebands, as

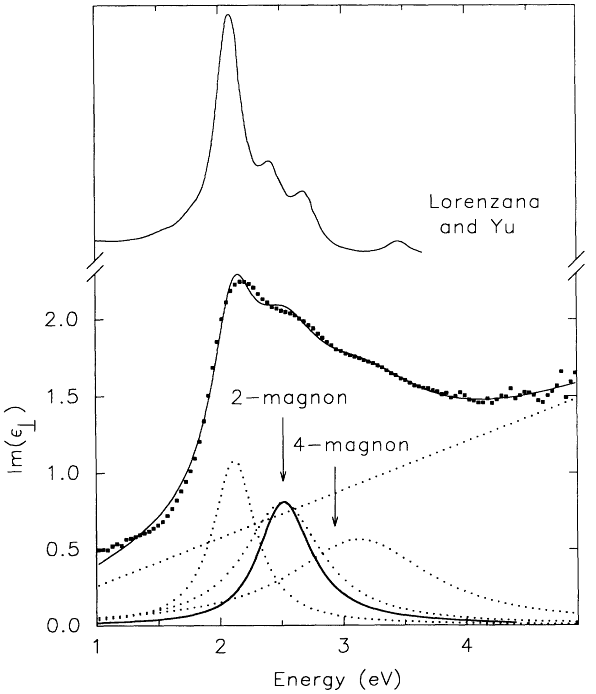

FIG. 5. Fit to $\mathrm{Im}(\varepsilon_\perp)$ using three Lorentz oscillators and a linear background term. Peaks are located at 2.11, 2.51, and 3.13 eV with widths (FWHM) of 0.42, 0.76, and 1.38 eV, respectively. The solid curve at the top, from Lorenzana and Yu (Ref. 20), is in arbitrary units and has been vertically offset for clarity. The bold curve is the calculated two-magnon line shape described in the text.

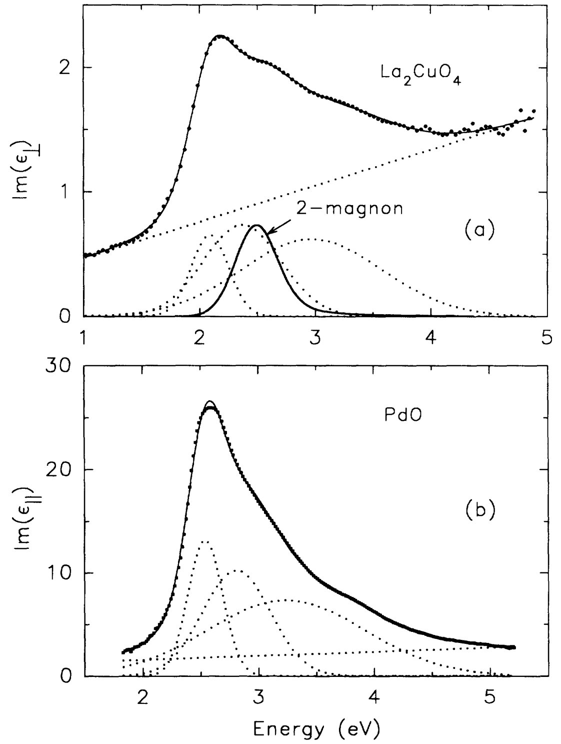

FIG. 6. (a) Fit to $\mathrm{Im}(\varepsilon_\perp)$ using three Gaussians and a linear background. Peaks are located at 2.09, 2.37, and 2.97 eV with widths of 0.38, 0.79, and 1.42 eV. The bold curve is calculated as in Fig. 5, but using the Gaussian line shape in the convolution. (b) Similar fit to $\mathrm{Im}(\varepsilon_\parallel)$ for PdO. Peaks are located at 2.54, 2.81, and 3.24 eV with widths of 0.35, 0.69, and 1.60 eV.

shown above, there is no evidence for a one-magnon sideband, which is the most prominent feature in the study by Perkins *et al.*[10] of the 0.4-eV exciton. A one-magnon excitation would be shifted up by ~0.19 eV, and there is clearly no room in our spectra for a large peak with this offset. The data of Falck *et al.*[12] also show no evidence for a one-magnon sideband, even though some of their measurements were done at lower temperatures where the main peak is narrower, which would make a sideband shifted by ~0.19 eV easier to see.

The results in Fig. 5 depend upon the arbitrary choice of Lorentzian line shapes. If we choose instead Gaussians, then with the same number of parameters the fit to the $\mathrm{Im}(\varepsilon_\perp)$ spectrum is much better, as shown in Fig. 6(a). In this case the second peak is shifted up by 0.28 eV from the CT excitation, which is midway between the energy expected for one- and two-magnon processes. Furthermore, the peak is now much broader than would be expected for the two-magnon feature, which is again shown as the bold curve. Thus, the use of Gaussian line shapes further weakens the argument for magnon sidebands.

As a final comment on the structure in $\mathrm{Im}(\varepsilon_\perp)$, we show in Fig. 6(b) comparable data for the oxygen *p* to metal *d* charge-transfer excitation in PdO.[28] In this material the Pd atoms are square-planar coordinated with four O atoms aligned parallel to the *c* axis, just as the Cu atoms are coordinated in the *a*-*b* planes of the high-T_c cuprates. Thus, $\varepsilon_\parallel$ in PdO is analogous to $\varepsilon_\perp$ in La_2CuO_4. Although the oscillator strength in PdO is much stronger, the general shapes of the bands are very similar, suggesting a common origin for the structure above the main transition. Since there are no magnetic interactions in PdO, this common origin cannot involve magnons.

In conclusion, we have measured the anisotropic dielectric response functions for single-crystal La_2CuO_4 from 0.7 to 4.9 eV. An analysis of our data indicates that the features above the charge-transfer excitation cannot be explained by multiple-magnon sidebands such as proposed by Perkins *et al.*[10] for the observed structure near 0.4 eV. In addition, our data do not agree with the line shape predicted by the theoretical calculations of Lorenzana and Yu.[20] It is more likely that the structure we observe simply arises from higher interband transitions such as proposed by Kircher *et al.*[32] for similar structure observed in $YBa_2Cu_3O_{7-\delta}$.

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