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THE ENERGY GAP IN THE HIGH-T_c COPPER OXIDE SUPERCONDUCTORS

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We briefly review high-resolution electron energy loss spectroscopy (HREELS) studies of the low energy excitations in the high-temperature superconductor $Bi_2Sr_2CaCu_2O_8$. HREELS has been used to determine the magnitude and temperature dependence of the energy gap (2Δ) for $Bi_2Sr_2CaCu_2O_8$ single crystals. Below the transition temperature low-energy excitations are detected in the energy loss spectra. Because the energy loss spectra are proportional to the real part of the frequency dependent resistivity, $\rho_R(\omega)$, the energy gap can be determined directly from the HREEL data. At low temperature $2\Delta = 6kT_c$ and Δ develops sharply for $T < T_c$. The constraints that these new results place on potential mechanisms of superconductivity are discussed.

1. Introduction

The magnitude, temperature dependence, and symmetry of the energy gap, $\Delta(T, k)$, for the high-temperature copper oxide superconductors remain the focus of intense investigation since $\Delta(T, k)$ provides essential insight into the microscopic mechanism of superconductivity. The magnitude of 2Δ determined from $YBa_2Cu_3O_{7-\delta}$ (YBCO)[1–5] and $Bi_2Sr_2CaCu_2O_{8+\delta}$ (BSCCO)[6–15] single crystals have spanned a wide range: $2\Delta = 0$–$12kT_c$. Several recent investigations seem to converge upon a value of $2\Delta = 6$–$8kT_c$,[1,3,6,9,10] although considerable controversy still exist concerning the nature of Δ.[2,15] Nevertheless, most of the reported values of 2Δ significantly exceed the weak-coupling BCS limit of $3.5kT_c$. A large value of the reduced energy gap, however, does not alone strongly constrain the mechanism of superconductivity since it could arise from a number of factors.

The temperature dependence and symmetry of Δ can provide much more powerful constraints on the mechanism of superconductivity, although there has been considerable experimental uncertainty in the details of $\Delta(T, k)$. Infrared (IR)[1] and high resolution electron energy loss spectroscopy (HREELS)[3] studies of YBCO have suggested that Δ is only weakly dependent on T, and surprisingly, that gap excitations do not disappear above T_c. Photoemission studies indicate that Δ may be weakly dependent on temperature for BSCCO samples,[8,9] although detailed analyses of the $\Delta(T)$ data have not been reported. Tunneling measurements suggest that $\Delta(T)$ in BSCCO is either BCS-like[13] or weakly dependent on temperature.[12] Hence, it has been essential to characterize unambiguously the magnitude and temperature dependence of 2Δ. In this report we briefly review our recent HREELS studies of BSCCO single crystals that provide a clear picture for the behavior of $\Delta(T)$ in high-temperature copper oxide superconductors. The review is organized as follows: in Sec. 1 we introduce the underlying theory for HREELS; in Sec. 3 we review and briefly discuss experimental studies of the BSCCO system; and in Sec. 4 we discuss the implications of these results in terms of several theoretical models for superconductivity.

2. Background to HREELS

The HREELS experiments were carried out using a fixed 90° scattering geometry, and collecting inelastically scattered electrons only within a 1–1.5° lobe of the elastically scattered beam.[3,6] In this regime of small momentum transfer ($q_{\|} = k'_{\|} - k_{\|} = 0.001$–$0.01 Å^{-1}$) dipole scattering theory can be used to quantitatively analyze the experimental energy loss spectra.[16,17]

In the context of dipole scattering theory the electron scattering probability in unit solid angle $d\Omega$ and unit energy $d(\hbar\omega)$ is

$$P(\mathbf{k},\mathbf{k}') = A(\mathbf{k},\mathbf{k}')(n_\omega + 1)\mathrm{Im}\ g(\omega, q_{\|}) \tag{1}$$

$A(k, k')$ is a kinematic term that depends only on the scattering geometry

$$A(\mathbf{k},\mathbf{k}') = \frac{2}{(ea_0\pi)^2}\frac{1}{\cos\alpha}\frac{k'}{k}\frac{q_{\|}}{(q_{\|}^2 + q_{\perp}^2)^2} \tag{2}$$

where α is the angle of incidence. n_ω is the Bose–Einstein factor,

$$n_\omega = \frac{1}{e^{\hbar\omega/k_{\mathrm{B}}T} - 1} \tag{3}$$

and Im g is the loss function. In general, the loss function is related to the dielectric properties of the material,

$$\mathrm{Im}\ g = \mathrm{Im}\ \frac{1}{1 + \varepsilon(\omega, q_{\|})}\,. \tag{4}$$

A specific model for $\varepsilon(\omega, q_{\|})$ is required to quantitatively calculate the loss function[3,16]; in general, $\varepsilon(\omega, q_{\|})$ can be written as a sum:

$$\epsilon(\omega, q_{\|}) = \epsilon_\infty + 4\pi i\frac{\sigma(\omega)}{\omega} + \frac{\omega_{\mathrm{p}}^2}{\omega_{\mathrm{TO}}^2 - \omega^2 - i\omega\Gamma(\omega)} \tag{5}$$

where $\sigma(\omega)$ is complex. The first term is simply the background dielectric of the material, the second term is the frequency dependent conductivity, the third term is due to phonon excitations.[16] We consider two limits here.

2.1. *The limit of high surface resistivity*

In the limit of high surface resistivity the second term does not contribute significantly to $\varepsilon(\omega, q_\parallel)$, and thus

$$\varepsilon(\omega, q_\parallel) = \varepsilon_\infty + \frac{\omega_p^2}{\omega_{TO}^2 - \omega^2 - i\omega\Gamma(\omega)} \tag{6}$$

where ω_{TO} is the transverse optical phonon, ω_p is the effective plasma frequency of the ions, and $\Gamma(\omega)$ is a damping function. A peak in the loss function will then occur at

$$\omega' = \omega_{TO}\left(\frac{\varepsilon(0)+1}{\varepsilon_\infty + 1}\right)^{1/2} \tag{7}$$

where $\varepsilon(0) = \varepsilon_\infty + \omega_p^2/\omega_{TO}^2$.

2.2. *The limit of high surface conductivity*

In the limit of high surface conductivity we ignore phonon contributions to the dielectric response and obtain

$$\varepsilon(\omega, q_\parallel) = \varepsilon_\infty + \frac{4\pi i\sigma(\omega)}{\omega}\,. \tag{8}$$

The loss function is $\mathrm{Im}\,(1/[1+\varepsilon_\infty + 4\pi i\sigma(\omega)/\omega])$, and in the limit of high conductivity this function reduces to

$$\mathrm{Im}\, g = \mathrm{Im}\,(\omega/4\pi i\sigma(\omega)) \equiv \frac{\omega}{4\pi}\rho_R(\omega) \tag{9}$$

where $\rho_R(\omega)$ is the real part of the frequency dependent resistivity. Since the superconducting energy gap (2Δ) can be determined directly from $\rho_R(\omega)$ (see below) HREELS represents an attractive approach for assessing 2Δ.

3. Experimental Data and Analysis

The BSCCO single crystals were grown from CuO rich melts as described previously.[18] Crystals obtained directly from the solidified melt, which are termed "as grown", typically have transition temperatures (T_c) between 82 and 85 K. The 90%–10% transition widths determined from magnetization data are large (10–20 K) for the as-grown crystals (Fig. 1). Large transition widths indicate that there is significant inhomogeneity (e.g., oxygen nonstoichiometry) in as-grown crystals.

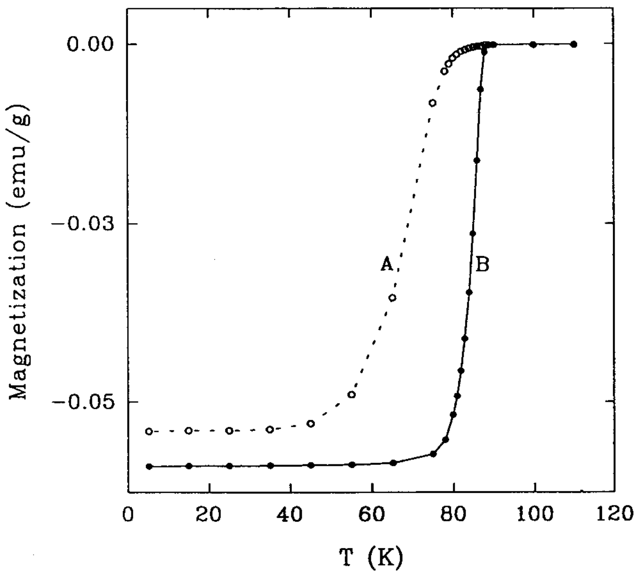

Fig. 1. Temperature dependent magnetization curves recorded in a field of 10 Oe on as-grown (A) and oxygen-annealed (B) BSCCO single crystals.

To avoid complications due to poor crystal quality we have also prepared significantly more homogeneous BSCCO crystals by careful oxygen annealing. Briefly, as-grown BSCCO crystals were annealed at 545°C in 12 atm O_2 for several days. These "oxygen-annealed" crystals exhibit a T_c of ≈ 90 K, and a transition width of 4–6 K (Fig. 1). These results show that the oxygen-annealed crystals are significantly more homogeneous than the as-grown crystals. These differences in crystal homogeneity lead to large variations in the observed HREEL spectra. A typical spectra recorded on an as-grown BSCCO single crystal is shown in Fig. 2. This spectrum exhibits three strong energy loss peaks (21, 48, and 79 meV) that correspond to bulk optical phonons in BSCCO. Bulk phonons are observed on high resistivity ($\rho \geq 1000$ $\mu\Omega$-cm) areas of the BSCCO surface. The cleaved as-grown crystals exhibit primarily high-resistivity surface termination and phonon structure. However, lower resistivity areas (10–100 $\mu\Omega$-cm) have been detected over ≈ 10% of surface by scanning the ≈ 70 μm diameter electron beam over the crystal. Since phonon peaks dominate the energy loss spectra of as-grown sample, it is very difficult to observe weak excitations corresponding to the energy gap. We believe that the previous difficulties[3,11] in observing 2Δ excitations by HREELS were due in large part to high resistivities typical of as-grown BSCCO surfaces.

In contrast, we have shown that cleaved oxygen-annealed crystals of BSCCO exhibit a high conductivity (10–100 $\mu\Omega$-cm) over most of the crystal surface. The

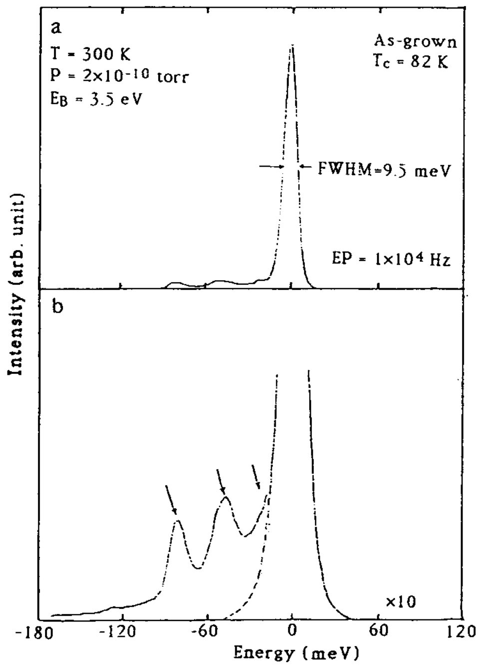

Fig. 2. (a) HREEL spectrum recorded on an as-grown BSCCO single crystal at 300 K using a electron beam energy (E_B) of 3.5 eV. The low intensity of the elastic peak (EP) and large FWHM are typical of samples with high surface resistivities. Small phonon features are visible in the energy loss spectrum between 10 and 20 meV. (b) An expanded view (10x) of the energy loss peaks corresponding to bulk phonons.

high-conductivity surfaces do not show phonon structure in the loss spectra. However, HREEL spectra recorded below the bulk crystal T_c do exhibit a broad energy loss feature centered at 60 meV (Fig. 3).[6] The intensity of this loss feature is $\approx$ 4000 times less than the quasielastic peak at 31 K. In addition, when the BSCCO sample temperature is increased above 31 K the intensity of the 60 meV loss feature decreases and then disappears when $T > T_c$. The 60 meV loss feature does reappear when the sample is again cooled below T_c. These temperature dependent changes in the energy loss spectra can thus be associated with pair-breaking excitations of energy 2Δ. Below we discuss the analysis of these data in greater detail.

In the high conductivity limit the experimental scattering probability is proportional to the real part of the frequency dependent resistivity, $\rho_R(\omega)$ (Eq. (9)). Hence, we can assign the magnitude of 2Δ to the onset of $\rho_R(\omega)$: for energies less than the gap $\rho_R(\omega) = 0$, but for $\omega > 2\Delta\, \rho_R(\omega)$ will be finite. In this respect HREELS measurements of 2Δ have many similarities with IR spectroscopy. HREELS does have several advantages versus IR spectroscopy, including (1) higher sensitivity, (2) a directly determination of $\rho_R(\omega)$ and (3) high spatial resolution.

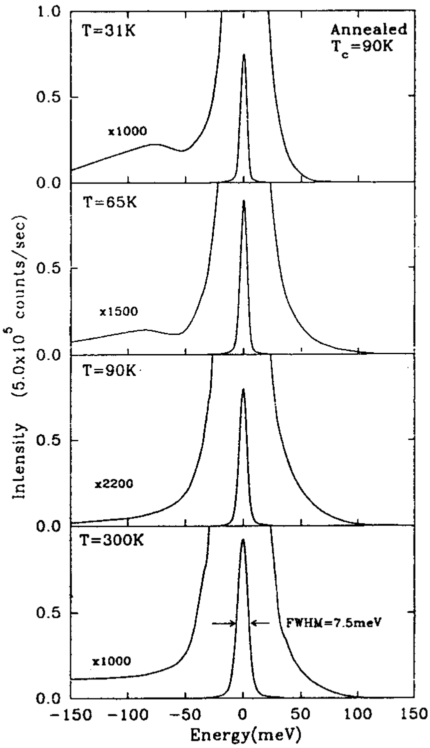

Fig. 3. Temperature dependent HREEL spectra recorded on an oxygen annealed BSCCO single crystal using a beam energy of 3.5 eV. The FWHM of the quasielastic peak at 0 meV is significantly smaller than in Fig. 2. At high sensitivity ($\geq$ 1000x) a temperature dependent energy loss feature is observed at −60 meV; this peak disappears above T_c.

To determine $\rho_R(\omega)$ we deconvolute the elastic peak from the spectra. The intensity of the resulting energy loss spectra is proportional to $\omega\rho_R(\omega)$; examples of the deconvoluted spectra shown in Fig. 4. The curves obtained from data recorded below T_c exhibit a clear onset to $\rho_R(\omega)$, while curves obtained from spectra recorded above T_c show very little frequency dependence. As discussed above the onset frequency corresponds to the energy gap. The magnitude of 2Δ obtained from our lowest temperature data (31 K) is 48 meV; this value corresponds to $2\Delta = 6.2\ kT_c$. The magnitude of 2Δ is significantly larger than predicted by the weak coupling BCS model, however, it is consistent with values obtained by photoemission spectroscopy.[7–10]

Although the magnitude of 2Δ is significantly larger than the weak coupling limit, the $\rho(\omega)$ versus ω curves (Fig. 4) bear a strong resemblance to the Mattis–Bardeen result for a BCS superconductor.[19] In Fig. 5, we quantitatively compare our 31 K experimental results to that calculated for a thermally broadened BCS

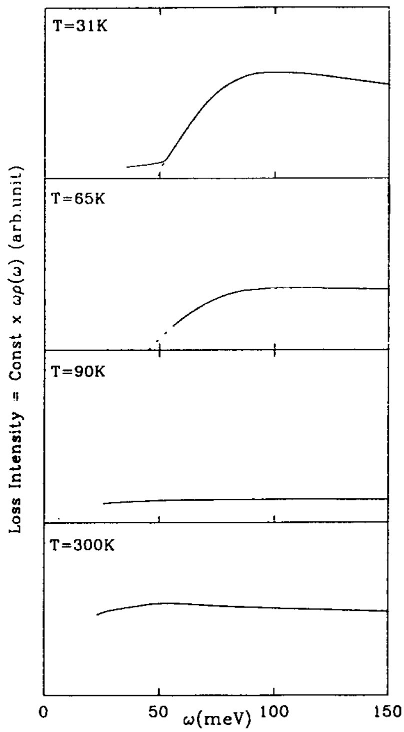

Fig. 4. Plots of the frequency dependent resistivity obtained by deconvoluting the quasielastic scattering peak from the HREEL spectra. A clear onset to $\rho_R(\omega)$ is observed in the plots obtained from data recorded below T_c.

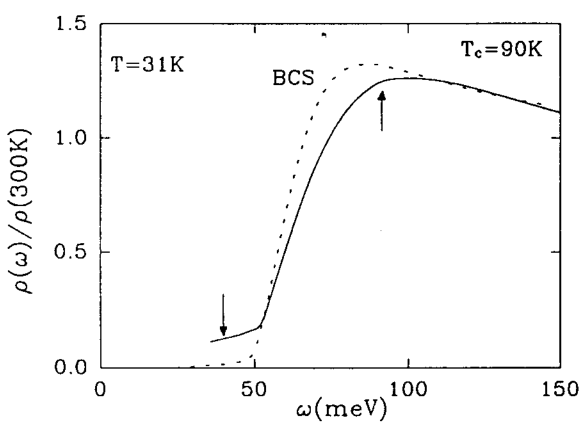

Fig. 5. Comparison of the normalized frequency dependent resistivity obtained from the experimental data (solid curve) and calculated by Mattis and Bardeen,[19] where $\rho_R = \sigma_1/(\sigma_1^2 + \sigma_2^2)$, and σ_1 and σ_2 are the real and complex parts of the frequency dependent conductivity, respectively.

superconductor with $2\Delta = 50$ meV. In general, these curves are similar, however, there are potentially important differences. Specifically, the experimental $\rho_R(\omega)$ curve deviates from the theoretical curve at the gap onset and at the gap edge (Fig. 5). The deviation at the gap edge (where $\rho_R(\omega)$ reaches a maximum) is reasonable since it is unlikely that the BSCCO crystals are in the clean limit. We believe, however, that the finite low-frequency resistivity tail does represent an important deviation from theory. Specifically, the low frequency tail in $\rho_R(\omega)$ suggests the presence of pair-breaking scattering in these materials (see below).

We have also been able to determine clearly the temperature dependence of the energy gap from the HREEL spectra. The experimental results are plotted in Fig. 6. From these data it is apparent that 2Δ depends weakly on temperature below T_c, although the gap does close rapidly at T_c.[6] A weak temperature dependence for 2Δ below T_c has also been reported in IR and HREEL spectroscopy studies of YBCO,[1,3] although the gap was found to persist above T_c in these latter studies. In the previous HREELS study of YBCO it is possible that the difference in the behavior of 2Δ near T_c could be attributed to irreversible surface degradation of YBCO, that is, oxygen is easily lost for the YBCO surface in vacuum. The BSCCO single crystals exhibit significantly greater stability than YBCO in vacuum.

Although it is unlikely that oxygen loss could explain the differences in our results with the IR studies of YBCO, strong background scattering in the IR measurements may obscure the intrinsic behavior of 2Δ near T_c. Regardless of the detailed origin of these differences, it is important to reiterate that our determination of 2Δ comes directly from the experimental data (since we measure $\rho_R(\omega)$), and that the sharp onset of 2Δ at T_c and the weak temperature dependence below T_c are reproducible.

4. Mechanistic Implications and Conclusions

Finally, we examine the implications of these HREELS measurements of $\Delta(T)$ in light of several existing models for superconductivity. First, it is readily apparent that weak coupling BCS theory[20] is inconsistent with the magnitude of Δ and the sharp opening of $\Delta(T)$ for $T < T_c$ (Fig. 6(a)). A strong- coupling model proposed by Arnold, Mueller, and Swihart provides an excellent fit to $\Delta(T)$ for $T < T_c$.[21] This model predicts, however, that Δ will persist above T_c, and is thus in disagreement with our experimental results since we find that the gap closes at T_c.[a] In contrast, there appears to be better agreement with recent models that consider strong pair-breaking interactions.[22,23] For example, the theory of Pines and coworkers, which is derived from an antiferromagnetically correlated Fermi-liquid, predicts both large values of $2\Delta/kT_c$ and a sharp development of Δ below T_c.[22] These results agree qualitatively with our experimental data. Bandte *et al.* have shown that dynamic

[a]The excellent agreement with our date below T_c suggests that additional investigation of this models[21] is warranted.

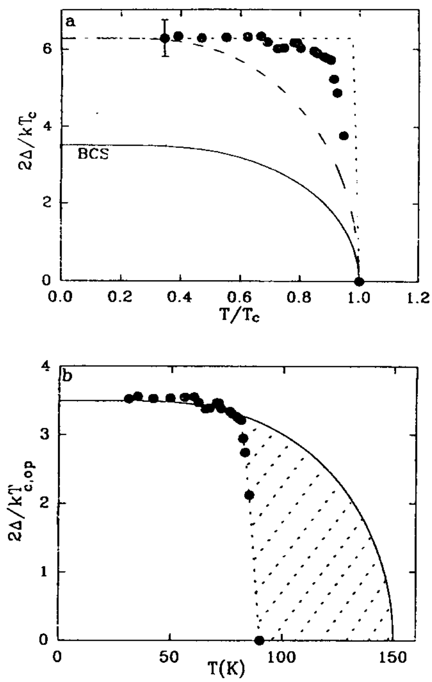

Fig. 6(a). Temperature dependence of the reduced gap. The experimental data corresponds to the solid circles. The solid curve is the behavior of $\Delta(T)$ predicted by BCS theory. The long dashed line curve corresponds to the behavior predicted by Pines and coworkers,[22] while the short dashed curve corresponds to the behavior predicted for dynamic pair-breaking.[23] (b) Plot of the experimental data (solid circles) scaled by T_c^* to yield a weak coupling limit for the reduced energy gap. The solid curve corresponds to the BCS prediction for $T_c^* \approx 150$ K. The hatched area between the experimental data points and the solid points represent the suppression of T_c by pair-breaking.

pair-breaking (e.g., single magnon scattering) can also yield a large value of $2\Delta/kT_c$ and a sharp development of Δ for $T < T_c$.[23] We compare the behavior of $\Delta(T)$ predicted by these two theories with our experimental results in Fig. 6(a). Both models show reasonable agreement with the experimental data, although neither theory reproduces all of the details in the experimental data. Nevertheless, we believe this similarity between theory and experiment suggests that the common physics (i.e., pair-breaking) in these models plays an important role in the BSCCO system. Additional evidence supporting the existence of strong pair-breaking is also evident from the tail in $\rho_R(\omega)$ at low frequencies (Fig. 5).

An important consequence pair-breaking is that it suppresses T_c from the value in the absence of scattering. Indeed, it is well-known that pair-breaking scattering processes will suppress T_c and $\Delta(0)$.[24,25] Since T_c is reduced more rapidly than $\Delta(0), 2\Delta(0) > 3.5kT_c$. The sharp onset of $\Delta(T)$ at T_c found in our experiments strongly indicates that such inelastic processes are important in BSCCO. Hence, it is interesting to speculate whether it is possible to obtain a higher or optimal transition temperature, T_c^*, in the absence of pair-breaking scattering. If we assume that the coupling interaction is weak, then T_c^* can be estimated from the weak coupling limit for the reduced energy gap $2\Delta/kT_c^* = 3.53$. Using the value of 2Δ determined in this study, we estimate that $T_c^* \approx 150$ K for the BSCCO system (Fig. 6(b)).[b] It will be interesting in the future to consider whether the spin excitation spectrum and inelastic scattering processes in BSCCO can be manipulated to reduce pair-breaking and enhance T_c.

In conclusion, we have used HREELS to determine the magnitude and temperature dependence of the energy gap. The energy loss spectra can be interpreted in a straightforward manner as frequency dependent resistivities, $\rho_R(\omega)$, and thus 2Δ is determined from the onset of $\rho_R(\omega)$. We have shown that at low temperature $2\Delta = 6kT_c$ and that Δ develops sharply for $T < T_c$. While these results are inconsistent with conventional theories, they strongly resemble the predictions of models that consider pair-breaking interactions. The similarity of $\Delta(T)$ to this latter work suggests that a higher T_c may be obtainable in these materials.

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[b] This suggestion can be tested by measuring $\Delta(0)$ in BSCCO samples with different T_cs. For example, increases in $2\Delta/kT_c$ as T_c is reduces would be consistent with out proposal.

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