Table I. Cell Parameters and Derived Oxygen Content (y) and Distribution [$P(0, {}^1/_2, 0$] for $YBa_2Cu_3O_y$ Ceramics[a]

ref	a, Å	b, Å	c, Å	y	$P(0, {}^1/_2, 0)$
Beech[2]	3.8250 (1)	3.8864 (1)	11.6945 (4)	6.47	0.90 (na)^N
Beech[2]	3.8198 (1)	3.8849 (1)	11.6762 (3)	6.81	0.93 (O_2)^N
Beno[3]	3.8231 (1)	3.8864 (1)	11.6807 (2)	6.73	0.92 (O_2)^N
Cava[4]	3.8218 (7)	3.8913 (7)	11.677 (2)	6.79	0.96 (O_2)^X
David[5]	3.8187 (2)	3.8833 (2)	11.6687 (6)	6.95	0.93 (O_2)^N
Engler[6]	3.820	3.894	11.688	6.59	0.99 (O_2)^X
Greedan[7]	3.816 (2)	3.892 (2)	11.682 (9)	6.70[b]	1.00[b] (O_2)^N
Hewat[8]	3.8206	3.8851	11.6757	6.82	0.92 (O_2)^N
Hyde[9]	3.820	3.886	11.703	6.31	0.93 (O_2)^X
Izumi[10]	3.8282 (2)	3.8824 (2)	11.6878 (5)	6.59	0.86 (O_2)^X
Izumi[11]	3.8223 (3)	3.8829 (3)	11.690 (1)	6.55	0.90 (O_2)^N
Kini[12]	3.826 (2)	3.889 (2)	11.673 (4)	6.87	0.91 (air)^X
Kini[12]	3.844 (4)	3.889 (4)	11.685 (8)	6.64	0.80 (O_2)^X
LePage[13]	3.827 (1)	3.877 (1)	11.708 (6)	6.21	0.83 (air)^X
Siegrist[14]	3.856 (2)	3.870 (2)	11.666 (3)	7.00[b]	0.59 (O_2)^X
Steinfink[15]	3.824 (1)	3.891 (1)	11.685 (2)	6.64	0.94 (air)^X
Strobel[16]	3.841 (5)	3.889 (4)	11.736 (7)	5.69	0.82 (q,air)^X
Strobel[16]	3.828 (3)	3.891 (2)	11.679 (4)	6.76	0.91 (O_2)^X

[a] Key: na, not annealed; air, annealed in air; O_2, annealed under O_2; q,air, quenched in air; N, neutron diffraction; X, X-ray diffraction. [b] Assumed.

Table II. Comparison of Observed and Calculated y and $P(0, {}^1/_2, 0)$ Values for Refined Neutron Diffraction Studies

	y		$P(0, {}^1/_2, 0)$	
ref	obsd	calcd	obsd	calcd
Beech[2]	~6.9	6.81	~1	0.93
Beno[3]	6.81	6.73	~1	0.92
David[5]	6.85	6.95	~1	0.93
Izumi[11]	6.69	6.55	0.91	0.90

[$P(0, {}^1/_2, 0) \simeq {}^1/_2$] should lead to a near equivalence of the a and b-axis lengths, to the limit of a tetragonal cell (probable space group $P4/mmm$). Thus, the difference in the a- and b-axis lengths can reasonably be taken as a measure of preferential site distribution. If one assumes (1) that the site preference is linear in the difference in the lengths of the a and b axes, (2) that only when $(b - a) = 0$ (tetragonal) is $P(0, {}^1/_2, 0) = {}^1/_2$ (by symmetry), and (3) that the site preference $P(0, {}^1/_2, 0) = 1$ (complete) for the determination of Greedan et al.;[7] then the very reasonable derived values, given the published preparative procedures,[2-16] for $P(0, {}^1/_2, 0)$ in Table I are obtained.

Similarly, if one assumes (1) that the sample of Siegrist et al.[14] has the formulation $YBa_2Cu_3O_7$ and that of Greedan et al.[7] is $YBa_2Cu_3O_{6.7}$ and (2) that there is a linear relationship between the length of the c axis and the total oxygen content; then the very rational values for y in Table I are derived.

To illustrate the utility and accuracy of the method, results from four powder neutron diffraction studies,[2,3,5,11] where oxygen atom site occupancies have been refined to give observed values (to an accuracy of about 0.04) for y and $P(0, {}^1/_2, 0)$, are compared to estimated values in Table II. In general, the calculated values for y and $P(0, {}^1/_2, 0)$ are in good accord with their experimental counterparts derived from the neutron results, strongly supporting the basic tenets of the method proposed here.

In summary, it is argued that if accurate cell constants are available (from X-ray, neutron, or electron diffraction), then semiquantitative estimates can be made for the oxygen atom site preference [$P(0, {}^1/_2, 0)$] and the total oxygen content (y) of a particular $YBa_2Cu_3O_y$ ceramic. Qualitatively, if the difference between the lengths of the b and a axes is large (~0.07 Å), then a strong preference [$P(0, {}^1/_2, 0) > 90\%$] is expected. If the difference in a and b is small (zero, in the limit of a tetragonal cell), then a weak site preference is anticipated [$P(0, {}^1/_2, 0) = {}^1/_2$ by symmetry in the limit of a tetragonal cell]. Additionally, if the c-axis length is small (~11.66 Å), then a formulation near $YBa_2Cu_3O_7$ is to be expected, with a diminishing oxygen content (y) denoted by an increasing c-axis length. Quite obviously, but apparently not always,[12] sample annealing in O_2 yields the highest total oxygen content (Table I). Finally, strong site preference [$P(0, {}^1/_2, 0) > 90\%$] is predicted (Table I) for properly annealed (O_2) samples.

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Electronic Structure and Fermi Level Location in Defect Superconducting Solids $YBa_2Cu_3O_{7-\delta}$ and $La_2CuO_{4-\delta}$

Sir:

The recently discovered[1-4] high-transition-temperature T_c superconducting materials $YBa_2Cu_3O_{7-\delta}$ and $(La,Sr)_2CuO_{4-\delta}$ are extraordinarily sensitive to the concentration of oxygen. The parent or undoped lanthanum compounds exhibit antiferromagnetism[5] and possibly superconductivity[5,6] at $\delta = 0.03$. With increasing δ the yttrium compounds show[7] a decrease in T_c. The superconductivity appears to vanish near or at $\delta = 0.5$, at which point the material is also no longer metallic. These observations have motivated us to examine the nature of the oxygen defects in these two systems.

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(1) Wu, M. K.; Ashburn, J. R.; Torng, C. J.; Hor, P. H.; Meng, R. L.; Gao, L.; Huang, Z. J.; Wang, Y. Q.; Chu, C. W. *Phys. Rev. Lett.* **1987**, *58*, 908.

(2) Cava, R. J.; Batlogg, B.; van Dover, R. B.; Murphy, D. W.; Sunshine, S.; Siegrist, T.; Remeika, J. P.; Rietman, E. A.; Zahurak, S.; Espinosa, G. P. *Phys. Rev. Lett.* **1987**, *58*, 1676.

(3) Grant, P. M.; Beyers, R. B.; Engler, E. M.; Lim, G.; Parkin, S. S. P.; Ramirez, M. L.; Lee, V. Y.; Nazzal, A.; Vazquez, J. E.; Savory, R. J. *Phys. Rev. B: Condens. Matter* **1987**, *35*, 7242.

(4) (a) Ganguly, P.; Raychaudhuri, A. K.; Sreedhar, K.; Rao, C. N. R. *Pramana* **1987**, *28*, 229. (b) Ganguly, P.; Mohan Ram, R. A.; Sreedhar, K.; Rao, C. N. R. *Pramana* **1987**, *28*, L321.

(5) Johnston, D. C.; Stokes, J. P.; Goshorn, D. P.; Lewondowski, T., to be submitted for publication.

(6) Grant, P. M.; Parkin, S. S. P.; Lee, V. Y.; Engler, E. M.; Ramirez, M. L.; Vasquez, J. E.; Lim, G.; Jacowitz, R. D.; Green, R. L. *Phys. Rev. Lett.* **1987**, *58*, 2488.

(7) Jorgensen, J. D.; Beno, M. A.; Hinks, D. G.; Sonderholm, L.; Volin, K.-J.; Hitterman, R. L.; Grace, J. D.; Schuller, I. K.; Segre, C. V.; Zhang, K.; Kleefisch, M. S., to be submitted for publication.

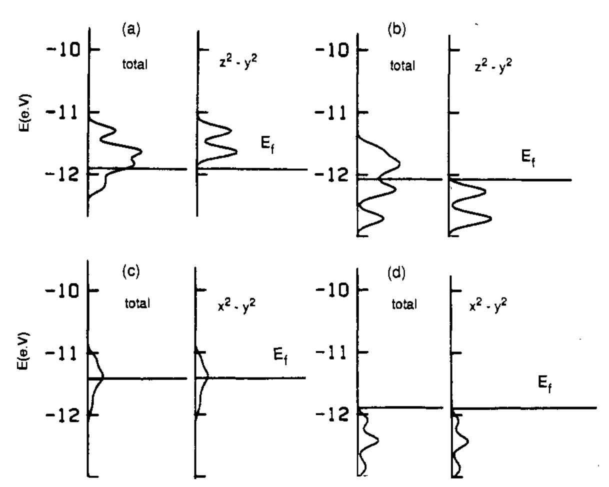
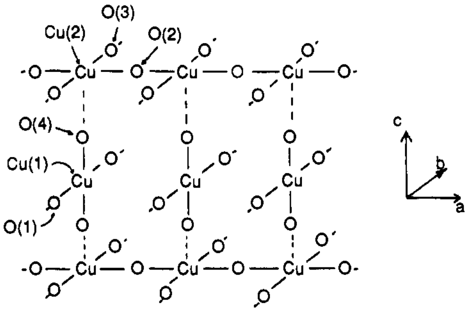


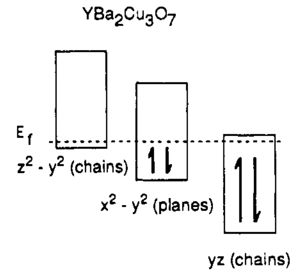
Figure 1. Total and partial electronic density of states for (a) the $Cu_3O_7^{7-}$ net in $YBa_2Cu_3O_7$ and (b) the $Cu_6O_{13}^{14-}$ net in $YBa_2Cu_3O_{6.5}$ where an oxygen atom is missing from O(1) as in case A and the CuO_4^{6-} net in (c) La_2CuO_4 and (d) $La_2CuO_{3.5}$. In the partial density of states notice the drop below the Fermi level of the $z^2 - y^2$ band of the copper atoms associated with the defect and also the change in $N(E_f)$.

Previous theoretical studies[8-11] have treated the defects in a rigid-band sense by adding 2δ electrons to the Fermi level of the structure calculated with $\delta = 0$. It is the purpose of this note to demonstrate that this is a poor approximation. This is a crucial point since the breakdown of rigid-band theory can have important consequences for the physical properties of these materials.

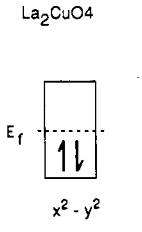


1

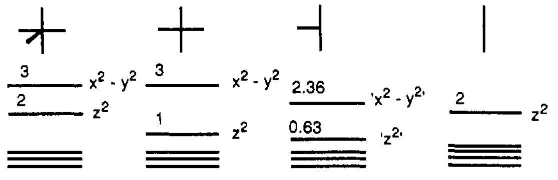
Neutron and X-ray diffraction show[12,13] that the structure of the material $YBa_2Cu_3O_7$ contains planes of square-planar copper atoms (CuO_2) that sandwich ribbons of square-planar copper atoms (CuO_3) as shown in **1**. There are long contacts from the oxygen atoms of the ribbons to the copper atoms of the planes resulting in square-pyramidal coordination for two-thirds of the copper atoms. In a formal sense the structure contains two Cu^{II} (the square pyramids) and one Cu^{III} (the squares). Recent in situ neutron diffraction measurements[7] as a function of temperature and oxygen partial pressure have demonstrated a transition from the orthorhombic to a disordered tetragonal phase at approximately 700 K. In the latter the oxygen concentration is 6.5 and the atoms in the chain are disordered so the O(1) sites are only partially occupied. Partial occupation of the previously empty O(5) sites, midway between Cu(1) chains, is also observed. It is in fact difficult to prepare the yttrium compounds without oxygen defects. The actual stoichiometry in the sample of ref 12 is $YBa_2Cu_3O_{6.84}$ where the oxygen vacancies are preferentially associated with the O(1) sites. From existing band structure computations on the material $YBa_2Cu_3O_7$, we may summarize[8-11] the basic electronic state of affairs as in **2a** with the aid of the energies of the molecular orbital levels of relevant metal coordination geometries shown in **3** using the parameters of the angular overlap model.[14] (For simplicity a σ-only model is used. The energies are in units of e_σ.) In rough terms there are four bands that intersect the Fermi energy. The $z^2 - y^2$ band of the square planes is nearly empty and the yz band of the square plane may be almost full, whereas the two (nearly degenerate) $x^2 - y^2$ bands of the square pyramids are slightly more or less than half full. This picture justifies the formal oxidation state assignments above. It is still open to some refinement, especially concerning the degree of participation of the orbitals located on the square planes at the Fermi level. The band structure of the La_2CuO_4 system is similar (**2b**) with exactly half-filled $x^2 - y^2$ bands for the stoichiometric material. The exact location of the energy bands of course depends on the interatomic distances. The diagrams of **3** are only to be used in a qualitative sense.



2a



2b



3

By performing tight-binding calculations along the lines of ref 11 for periodic defect structures with $\delta = 0.5$, we study the effects of various oxygen defects on the electronic properties of both of these systems. Four distinct cases are considered. In all cases the band shape and/or Fermi energy changes appreciably due to shifts in position of the molecular orbitals. Experimentally,[7] for $YBa_2Cu_3O_{7-\delta}$ it appears that the O(1) atoms are the ones most readily removed. If one O(1) atom is lost per unit cell doubled along *b* (case A), then each of the copper atoms associated with the defect (two of them) lie in a T-shaped environment. Now two $z^2 - y^2$ orbitals drop to lower energy (**3**), but only two extra electrons are present to fill them. Thus loss of an oxygen atom in this way will result in depression of the Fermi level, since electrons are drained away from the HOMO's of the Cu^{II} atoms. The computed values of the Fermi level (from the orbital parameters of ref 11 and the geometry of ref 12) are −12.079 and −11.904 eV for case A and the parent, respectively. There is a drop in the Fermi energy density of states $N(E_f)$ to about half the value found for the parent. However, loss of this oxygen atom to give an equal mixture of square-planar (Cu^{III}) and linear two coordination (Cu^{I}) in chains that alternate in character along *a* (case B) will result in no change in the Fermi level location (calculated to be −11.904 eV) since now only one atom per doubled

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(8) Mattheiss, L. F.; Hamann, D. R., submitted for publication.

(9) Massidda, S.; Yu, J.; Freeman, A. J.; Koelling, D. D., submitted for publication in *Phys. Lett.*

(10) Yu, J.; Massidda, S.; Freeman, A. J.; Koelling, D. D., submitted for publication in *Phys. Lett.*

(11) Whangbo, M.-H.; Evain, M.; Beno, M. A.; Williams, J. M. *Inorg. Chem.*, in press.

(12) Beno, M. A.; Soderholm, L.; Capone, D. W.; Hinks, D. G.; Jorgensen, J. D.; Schuller, I. K.; Segre, C. U.; Zhang, K.; Grace, J. D., submitted for publication in *Appl. Phys. Lett.*

(13) Siegrist, T.; Sunshine, S.; Murphy, D. W.; Cava, R. J.; Zahurak, S. M. *Phys. Rev. B*: *Condens. Matter* **1987**, *B35*, 7137.

(14) Schuller, I. K.; Hinks, D. G.; Beno, M. A.; Capone, D. W.; Soderholm, L.; Loquet, J.-P.; Bruynseraede, Y.; Segre, C. U.; Zhang, K., submitted for publication in *Solid State Commun.*

(15) These levels are shown in: Burdett, J. K. *Molecular Shapes*; Wiley: New York, 1980. The orbital labels for the T-shape geometry are not as straightforward as we have shown, since here z^2 and $x^2 - y^2$ mix together in this low-symmetry environment.

unit cell contains a deep-lying $z^2 - y^2$ orbital with two electrons to fill it. Here we calculate virtually no change in $N(E_f)$. Parts a and b of Figure 1 show a computed density of states and their orbital composition for the parent with $\delta = 0$ and a periodic solid for case A (with $\delta = 0.5$). Although the structure at $\delta = 0.5$ is disordered,[7] we find case B, with its linear Cu^I atoms, to be the more attractive from a chemical point of view.

These ideas then suggested that the real situation is much more complex than that suggested earlier by using a rigid-band model with the $y = 7$ parent. Since the exact location of the $z^2 - y^2$ band relative to $x^2 - y^2$ is open to question (a small parameter change would drop its energy enough to be partially filled at $\delta = 0$), the extent of filling of this band, probably crucial for the superconducting properties, will depend very much on the nature of these defects.

There are other sites that in principle may be associated with the defects. Analysis of these generates pictures that are is very similar for both the $YBa_2Cu_3O_{7-\delta}$ and $(La,Sr)_2CuO_{4-\delta}$ systems. Removing a single oxygen atom (O(2) or O(3)) associated with the copper atoms in one of the CuO_2 planes in a $YBa_2Cu_3O_7$ cell, which is doubled along either *a* or *b* respectively (Case C), will result in a marked drop of the half-full $x^2 - y^2$ orbitals associated with the two atoms to which the oxygen is coordinated (see 3). Since loss of this oxygen atom gives rise to a T-shaped geometry at two copper atoms, with deeper lying and now doubly filled $x^2 - y^2$ and z^2 orbitals there is no change (unless we let the geometry relax) of the Fermi level of the material. (We calculate −11.095eV). Two half-filled orbitals drop below the Fermi level and two extra electrons come via the defect to fill them completely, and from the calculation, $N(E_f)$ is halved. Two Cu^{II} atoms have now become Cu^I. Removal of every O(2) or O(3) atom along either *a* or *b* respectively in one of the CuO_2 sheets (case D) leads to a single two-coordinate copper atom per doubled cell. Since the $x^2 - y^2$ orbital associated with it drops in energy (3), and is now doubly filled, an extra electron gets added at the Fermi level, which should rise. The effect is half as large as expected on the rigid band model. The Fermi level is computed to lie at −11.787eV for this case. Here is no change in $N(E_f)$. This result is directly applicable to $La_2CuO_{4-\delta}$. Although it is not exactly clear where the loss of oxygen atoms occurs here, removal of an in-plane oxygen leads to an analysis similar to the one we have just shown. For case A′ (the equivalent of case A above) for $\delta = 0.5$ we show in Figure 1c,d the change in the shape and location of the density of states at the Fermi level. In this arrangement all the copper atoms (now Cu^I) are T-shaped, $x^2 - y^2$ has dropped dramatically as a result (see 3), and the Fermi level has dropped by about 0.5 eV to the top of this band. Thus the presence of in-plane defects in concentrations smaller than those used here just removes levels from the $x^2 - y^2$ band with a corresponding decrease in $N(E_f)$.

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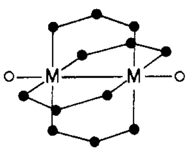
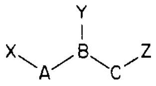
Synthesis and Molecular Structure of a Dinuclear Quadruply Bridged Cobalt(II) Compound with a Short Metal–Metal Bond, $Co_2[(p\text{-}CH_3C_6H_4)NNN(p\text{-}C_6H_4CH_3)]_4$

Sir:

There are many environments of ligand atoms in which M–M bonds of order 1–4 may exist,[1] but undoubtedly the type of most general importance is that shown schematically in I. The M_2 unit is embraced by a set of four bent, triatomic, bidentate ligands, usually carrying a charge of −1 (or −2), arranged in a paddle-wheel or lantern pattern. There may also be two additional ligands in axial positions, but not necessarily. A more detailed but general representation of the bidentate ligand is II. The commonest ligands are carboxylate ions, but other important ones include amido anions, $RNC(R')O^-$, amidinato ions, $RNC(R')NR''^-$, triazenato ions, which are usually of the symmetrical type, $RNNNR^-$, and yet others.



I



II

It is well-known that because of the different electronic properties of these ligands they have quite different effects on the stabilities, oxidation potentials, spectra, etc. of the M_2 unit they encapsulate. As a generalization, the more basic ligands, viz. $RNNNR^- \approx RNC(R')NR^- > RNC(R')O^- > OC(R)O^-$, seem to lend greater stability to a given M_2^{4+} unit; i.e., they strengthen the metal–metal interaction and also stabilize it in higher oxidation states.[2]

In recent work from this laboratory, we have exploited this property to obtain new M_2 compounds of the type $M_2[(p\text{-}CH_3C_6H_4)NCHN(p\text{-}C_6H_4CH_3)]_4{}^{n+}$, with M = Ni, Pd, Ir and n = 0, 1.[3,4] We have attempted to employ the same ligand to synthesize the corresponding cobalt compound, but without success. However, we can now report that with the $(p\text{-}CH_3C_6H_4)NNN(p\text{-}C_6H_4CH_3)^-$ ligand the dicobalt(II) compound has been prepared and characterized chemically and structurally.

Low-temperature (−78 °C) interaction of anhydrous $CoCl_2$ with 2 equiv of Li^+triaz^-, where triaz = $(p\text{-}CH_3C_6H_4)NNN(p\text{-}C_6H_4CH_3)$, prepared in situ from Htriaz and *n*-BuLi, in THF as solvent, immediately afforded $Co_2(triaz)_4$ (eq 1) as a brown microcrystalline solid that contains interstitial THF molecules.

$$2CoCl_2 + 4Li^+triaz^- \xrightarrow[-78\ °C]{THF} Co_2(triaz)_4 + 4LiCl \qquad (1)$$

These are easily lost (at least partially) upon separation of the solid from its mother liquor, and an accurate elemental analysis could not therefore be obtained.

The ^1H NMR spectrum taken on a vacuum-dried sample indicates that this is a diamagnetic compound with a formula close to $Co_2(triaz)_4{\cdot}7THF$.[5] The product is fairly stable at room temperature, although long storage of solid samples and of its solutions under argon at the laboratory temperature resulted in the production of blue insoluble material, presumably oligomeric $Co(triaz)_2$ containing tetrahedrally coordinated cobalt(II) ions. It is extremely sensitive to moisture, with decomposition to Htriaz and $Co(OH)_2$, as shown by IR spectroscopy. Recrystallization

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(1) Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*; Wiley: New York, 1982.
(2) (a) Duncan, J.; Malinski, T.; Zhu, T. P.; Hu, Z. S.; Kadish, K. M.; Bear, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 5507. (b) Le, J. C.; Chavan, M. Y.; Chau, L. K.; Bear, J. L.; Kadish, K. M. *J. Am. Chem. Soc.* **1985**, *107*, 7195. (c) Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A.; Tocher, J. H. *Inorg. Chim. Acta* **1985**, *101*, 185. (d) Tocher, D. A.; Tocher, J. H. *Inorg. Chim. Acta* **1985**, *104*, L15. (e) Tocher, D. A.; Tocher, J. H. *Polyhedron* **1986**, *5*, 1615.
(3) Cotton, F. A.; Poli, R. *Polyhedron* **1987**, *6*, 1625.
(4) Cotton, F. A.; Matusz, M.; Poli, R.; Feng, X. *J. Am. Chem. Soc.*, in press.
(5) Spectral data for $Co_2(triaz)_4{\cdot}7THF$ is as follows. ^1H NMR (C_6D_6, δ): 6.86 (dd, C_6H_4, 32 H), 3.46 (s, br, ca. 30 H), 1.97 (s, CH_3, 24 H), 1.32 (s, br, ca. 26 H). Weak peaks at 9.43 (s), 7.50 (s, br), and 2.19 (s) were also present and were attributed to free Htriaz. IR (Nujol mull, cm^{-1}): 3020 m, 1605 m, 1500 s, 1410 w, 1380 w, 1300 vs, 1260 vs, 1165 w, 1110 w, 1045 m, 1010 w, 890 w, 825 ms, 755 w, 715 w, 660 m, 625 w, 525 m, 495 w.

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