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Neutron scattering studies of the magnetic structure of cupric oxide

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In light of the recent discovery of copper oxide high-T_c superconductors, we have reexamined the early neutron diffraction measurements on CuO by Brockhouse [B. N. Brockhouse, Phys. Rev. **94**, A781 (1954)]. Our measurement confirmed the antiferromagnetic ordering in CuO below 225 K. The magnetic unit cell has a volume double that of the chemical unit cell. The ordered moment is $0.68\mu_B$ per Cu, significantly smaller than $1\mu_B$ expected for a spin-only Cu^{2+} ion. The diffuse scattering was also studied well above the Néel temperature, and was found to be mostly elastic, in clear contrast to that of La_2CuO_4.

I. INTRODUCTION

The Cu^{2+} ion has been of considerable interest in studies of magnetism. In crystal environments, the orbital moment of the Cu^{2+} ion ($L=2$) is almost completely quenched, and the ion behaves like an isotropic "spin-only" system ($S=\frac{1}{2}$). Typical g values, as measured in many experiments, are close to 2. Hence, the ion is often found in antiferromagnetic Heisenberg systems, especially those of one and two dimensions.[1] In many of these systems, the magnetic interactions between the Cu^{2+} ions are enhanced in one or two directions through superexchange due to the intervening anions. However, there has been little work performed on the oxide CuO, except for the study briefly reported by Brockhouse.[2]

The discovery of antiferromagnetism[3–5] in La_2CuO_4 has encouraged speculation that magnetic interactions may be important for electron pairing in $La_{2-x}A_xCuO_4$ ($A=$Ba, Sr, Ca) superconductors. A recent report[6] of strong two-dimensional magnetic correlation within the CuO_2 planes in La_2CuO_4 at temperatures well above the Néel temperature has generated further excitement. As CuO_2 planes are also common to the structure of the $RBa_2Cu_3O_7$ (R is almost any rare earth) family of superconductors, one may anticipate that magnetic interactions involving Cu and O ions are relevant to all copper oxide superconductors. To help characterize the magnetic behavior intrinsic to copper oxide systems, we have undertaken a neutron scattering study of antiferromagnetism in cupric oxide (CuO), one of the few magnetic copper oxides which do not contain other magnetic atoms.

Cupric oxide occurs in nature as paper-thin twinned aggregates. It is a steel grey to black stoichiometric semiconductor. Specific-heat measurements[7] (Fig. 1) first indicated that it undergoes an antiferromagnetic transition at a temperature of about 220 K. A neutron diffraction experiment by Brockhouse[2] verified this speculation and set the lower limit of the ordered moment at $0.5\mu_B$ per Cu ion. The magnetic susceptibility measurement[8] (Fig. 1), however, showed a somewhat unusual behavior: The susceptibility continues to rise above the Néel temperature and does not reach its maximum until 540 K. O'Keeffe and Stone[8] used a molecular antiferromagnetism (i.e., noncooperative) model to account for this broad maximum. The crystal structure does not seem to support their interpretation, however, as the Cu ions sit at symmetry sites in the crystal and are equally spaced from one another along the $[10\bar{1}]$ direction in which the

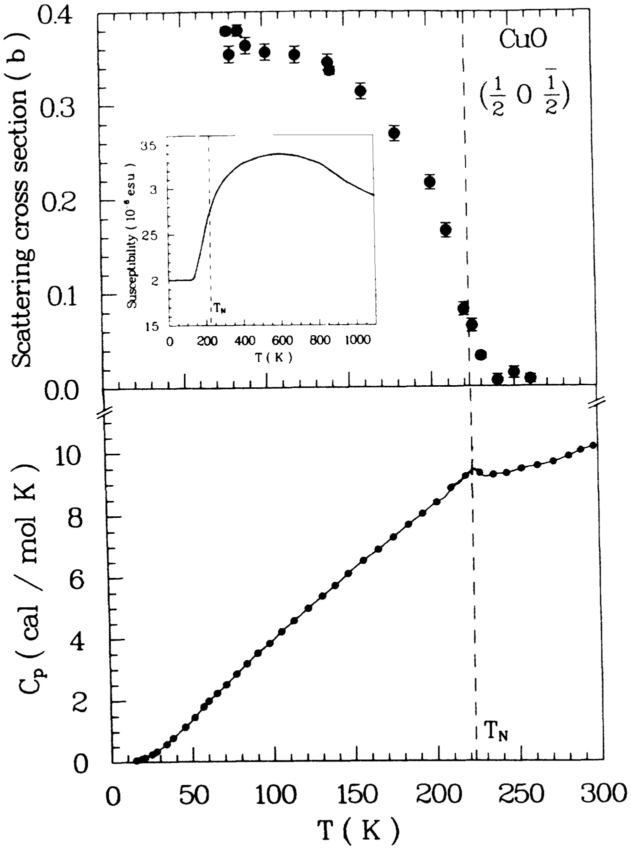

FIG. 1. Magnetic properties of CuO vs temperature. Top panel: the integrated intensity of the $(\frac{1}{2}0\bar{\frac{1}{2}})$ magnetic peak as a function of temperature. Bottom panel: the specific heat data (Ref. 7). Inset: the magnetic susceptibility (Ref. 8).

TABLE I. Atomic positions in CuO. The structure is monoclinic, with space group $C2/c$ and lattice parameters $a = 4.6837$ Å, $b = 3.4226$ Å, $c = 5.1288$ Å, and $\beta = 99.54°$ and 20 °C, as determined in Ref. 10. The value $y = 0.4161(20)$ obtained in this work may be compared with the values 0.416 (Ref. 9) and 0.4184(13) (Ref. 10) of previous work.

Cu in 4(c)	
(1)	$(\frac{1}{4},\frac{1}{4},0)$
(2)	$(\frac{3}{4},\frac{3}{4},0)$
(3)	$(\frac{3}{4},\frac{1}{4},\frac{1}{2})$
(4)	$(\frac{1}{4},\frac{3}{4},\frac{1}{2})$
O in 4(e)	
(1)	$(0,y,\frac{1}{4})$
(2)	$(\frac{1}{2},\frac{1}{2}+y,\frac{1}{4})$
(3)	$(0,-y,\frac{3}{4})$
(4)	$(\frac{1}{2},\frac{1}{2}-y,\frac{3}{4})$

superexchange most likely occurs.

The crystal structure of CuO has been studied by x-ray diffraction.[9,10] Åsbrink and Norrby[10] did a careful refinement with a diffraction pattern containing 225 peaks from a single crystal. Unlike the usual rock-salt structure of other $3d$ transition-metal monoxides, the structure of CuO is in the monoclinic space group $C2/c$ (no. 15, $a = 4.6837$ Å, $b = 3.4226$ Å, $c = 5.1288$ Å, and $\beta = 99.54°$ at 20 °C) with four formula units per unit cell. Copper ions occupy symmetry site 4(c) which contains no adjustable parameters (see Table I). Oxygen atoms, on the other hand, take position 4(e) which may be adjusted to give the correct intensity distribution in a diffraction experiment.

II. EXPERIMENT

The CuO powder was obtained from Aesar (purity 99.99%) and used without further purification. The cylindrical sample (about 50 mm in length and 12 mm in diameter) was pelletized and then sintered in air at 950 °C for 20 h. It was then sealed in an aluminum can which was back-filled with ^{4}He gas, and mounted on the cold finger of a cryostat operated with liquid nitrogen. The temperature was controlled from 78 to 260 K to within 1 K by regulating the heater current supplied to the cold finger and the flow rate of the nitrogen vapor. For measurements at and above room temperature, a furnace was used and the sample was kept in air to avoid decomposition.

Neutron scattering measurements were made on the H7 triple-axis spectrometer at the Brookhaven high flux beam reactor (HFBR) using 13.7-meV neutrons. The (002) reflection of pyrolytic graphite (PG) was used for both monochromator and analyzer, spectrometer collimation was chosen to be 20′-40′-20′-40′, and two PG filters were inserted before and after the sample to suppress higher-order contamination of the beam. The intensity of the second-order neutrons is estimated to be below 10^{-5} of that of the first order. Measurements using polarized neutrons and polarization analysis were made on spectrometer H8, which is equipped with Heusler alloy monochromator and analyzer crystals. The neutron energy for the polarized-beam work was 41 meV.

III. RESULTS AND DISCUSSION

We first performed diffraction measurements at 260 K, above the Néel temperature. The positions of 15 observed nuclear peaks with $Q < 4.5$ Å^{-1} agree well with those calculated from the known lattice constants.[10] The oxygen position parameter was adjusted slightly in order to fit the observed intensity distribution of these peaks. The result, $y = 0.4161(20)$, is consistent with an earlier work,[9] but differs slightly from that of Åsbrink and Norrby.[10] The overall agreement between the calculated and the observed intensity is satisfactory:

$$R \equiv \sum | I_{\rm calc} - I_{\rm expt} | / \sum I_{\rm expt} = 0.027 \ .$$

We next measured the magnetic scattering below the Néel temperature. Figures 2(a) and 2(b) show the spectrometer scans taken at 78 and 260 K. In the low-temperature spectrum, weak superlattice reflections are observed, the strongest of which, the $(\frac{1}{2}0\bar{\frac{1}{2}})$, has a peak intensity 6.5% of that observed for the (111) nuclear peak; the other superlattice peaks are at the 1–2 % intensity level. The temperature dependence of the $(\frac{1}{2}0\bar{\frac{1}{2}})$ peak shown in Fig. 1 was also observed in polarized-beam measurements, thus verifying its magnetic origin. Due to the weak magnetic scattering and the relatively high density of nuclear peaks at larger Q, it was not possible to obtain useful measurements for magnetic peaks beyond those shown in Fig. 2. We have indexed the magnetic peaks in terms of the reciprocal lattice parameters of the chemical cell. The half-integer indices h and l indicate a doubling of the lattice periodicity along the a and c axes due to antiferromagnetic ordering of the Cu moments. We observed that while all the peaks with index $h + l =$ even integers are present, those with $h + l =$ odd integers are completely missing.

A general expression for the magnetic structure factor is given by the following expression:

$$|F_m|^2 = \frac{\gamma_0^2}{4} M_{\rm eff}^2 |f(Q)|^2 \left| \sum_j \hat{\mathbf{S}}_{j\perp} e^{i\mathbf{Q}\cdot\mathbf{R}_j} \right|^2 . \tag{1}$$

Here, $\gamma_0^2 = 0.291$ b$/\mu_B^2$, $M_{\rm eff}$ is the effective moment per ion, $\hat{\mathbf{S}}_j$ is the unit vector along the moment of the jth Cu ion, $\hat{\mathbf{S}}_{j\perp}$ is the component of $\hat{\mathbf{S}}_j$ perpendicular to the scattering vector $\mathbf{Q}$, $f(Q)$ is the magnetic form factor of Cu^{2+}, and the sum is performed over all Cu ions in the magnetic unit cell. In a powder diffraction experiment, this formula has to be averaged over all equivalent crystal orientations. For collinear systems the expression for the average intensity is greatly simplified,[11]

$$|F_m|^2 = \frac{\gamma_0^2}{4} M_{\rm eff}^2 |f(Q)|^2 \left| \sum_j e^{i\mathbf{Q}\cdot\mathbf{R}_j} \right|^2 [1 - \langle(\hat{\mathbf{Q}}\cdot\hat{\mathbf{S}})^2\rangle] \ . \tag{2}$$

The systematic absence of magnetic peaks with

$h+l=$odd integer cannot be due to a special spin orientation, since the corresponding **Q** vectors point in various different directions relative to the direct lattice, not all of which can be parallel to a unique spin direction. From Eq. (1) we deduce that in order to produce such a diffraction pattern, Cu moments must be arranged in such a way that the moments of Cu(1) and Cu(3) are identical in both direction and magnitude, while the moment of Cu(2) should be the same as that of Cu(4) in amplitude but opposite in direction.

Since only a few good magnetic peaks have been measured, we feel that it is not meaningful to pursue a complex model. We thus assumed that all copper spins are collinear and are of the same amplitude. The spin arrangement shown in Fig. 3 gives the correct selection rule: The moments of Cu(1), Cu(3), and Cu(4) point to the same direction while that of Cu(2) points to the opposite. The spins occupying the same position in the next chemical unit cells along the a or c axis are in the opposite direction. In this structure, the Cu-O-Cu chains along the $[10\bar{1}]$ direction are completely antiferromagnetically arranged. Table II lists the observed intensities of the magnetic peaks, together with calculated intensities for two likely spin orientations. The best fit to the data is obtained with the spins along the [111] direction. In our spectrum (Fig. 2), three peaks $[(\frac{1}{2}0\frac{\bar{1}}{2})$, $(\frac{1}{2}0\frac{3}{2})$, and $(\frac{1}{2}1\frac{3}{2})]$ stand alone, and their areas can be determined fairly reliably. Two other peaks $[(\frac{3}{2}0\frac{1}{2})$ and $(\frac{3}{2}1\frac{1}{2})]$ are not completely resolved from adjacent nuclear Bragg peaks and their areas were obtained after subtraction of the data obtained at a much higher temperature (260 K). These numbers inevitably contain larger errors and therefore we have doubled their statistical errors in Table II. The weakest peak in the spectrum, $(\frac{1}{2}1\frac{\bar{1}}{2})$, happens to be on top of a broad peak likely due to contamination. We can-

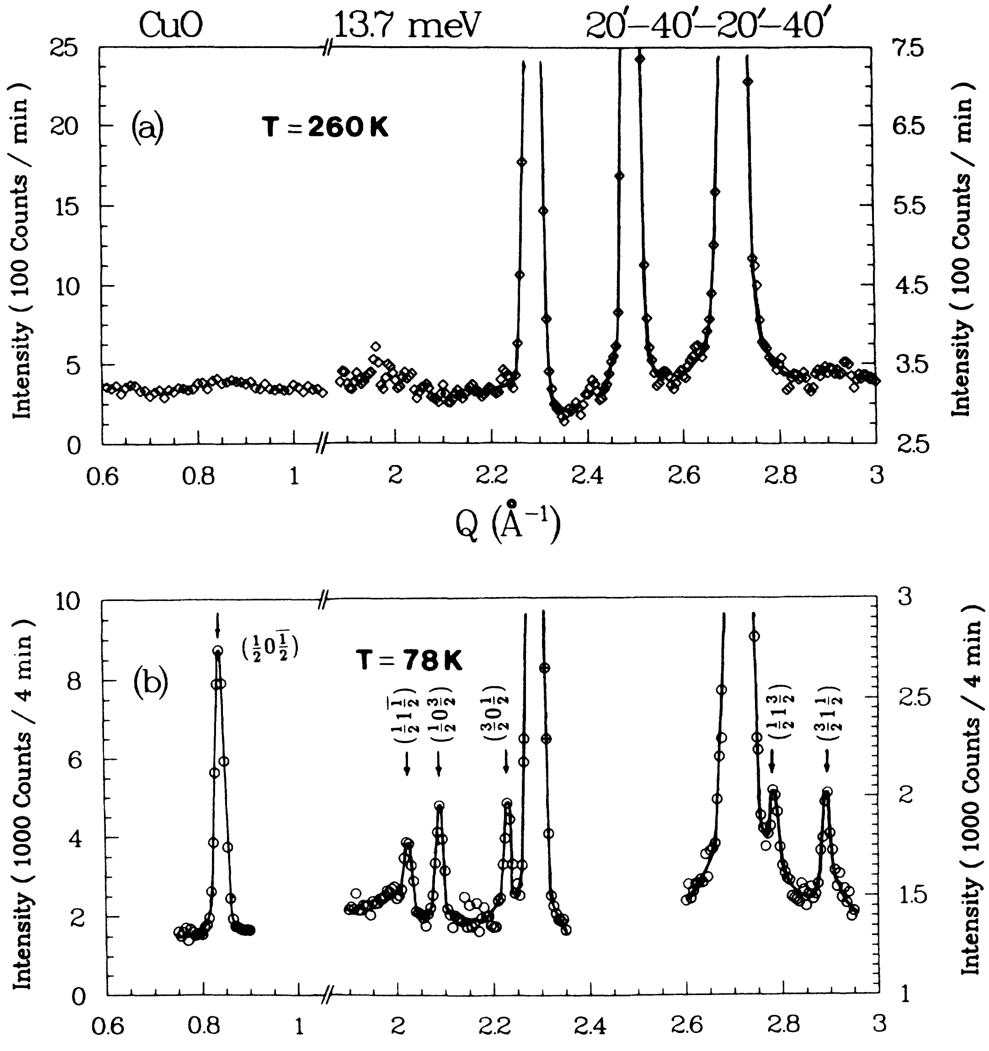

FIG. 2. Diffraction spectra around the magnetic lines (a) at 260 K, and (b) at 78 K. The lines are drawn to guide the eyes. Note that the scales are different for the left and the right halves of the spectra. The intensity of the (111) peak at $Q=2.71$ Å^{-1} is 3.41×10^4 counts/min at 260 K.

TABLE II. Intensities of the magnetic peaks, normalized to that of the $(\frac{1}{2}0\frac{\bar{1}}{2})$. The two sets of calculated intensities are based on the assumption that the spins are (1) along the [010] direction or (2) along the [111] direction. The values in parentheses after the experimental intensities are estimated errors of the measurement.

Peak	Q (Å^{-1})	I_{calc} (1)	(2)	I_{expt}
$(\frac{1}{2}0\frac{\bar{1}}{2})$	0.842	1.000	1.000	1.000(12)
$(\frac{1}{2}1\frac{\bar{1}}{2})$	2.020	0.048	0.172	<0.060
$(\frac{1}{2}0\frac{3}{2})$	2.087	0.127	0.070	0.077(7)
$(\frac{3}{2}0\frac{1}{2})$	2.229	0.107	0.057	0.069(22)
$(\frac{1}{2}1\frac{3}{2})$	2.779	0.066	0.064	0.068(22)
$(\frac{3}{2}1\frac{1}{2})$	2.888	0.063	0.057	0.079(8)

not estimate its area reliably, and have lowered its weight in the model fit. The level of agreement between the observed intensities and those calculated for a [111] spin direction is fair but less than overwhelming. The calculations, of course, depend to some degree on the assumption made for the magnetic form factor[12] of Cu; however, we consider it unlikely that improved knowledge of the form factor would make a significant difference in the quality of the fit. At this point, we cannot eliminate the possibility that a more complex spin arrangement exists in CuO. This will be the subject of future single crystal experiments.

An important question, relevant to the copper oxide superconductors, concerns the effective moment on a copper ion. In a crystal field with tetragonal symmetry or lower, the ground state of Cu^{2+} is normally an orbital singlet ($L=0$). The g factor departs slightly from the free spin value of 2 since spin-orbit coupling mixes some other orbital states.[18] Typically, this effect changes the g factors by about 10–20%, and one would expect a moment $M_{\text{eff}}=g\langle S\rangle=1.1\mu_B$. The actual value of $\langle S\rangle$ is reduced by covalency effects and spin fluctuations. Using the form factor data[12] obtained in K_2CuF_4, a well-studied two-dimensional ferromagnet, we deduced an ordered moment of $(0.68\pm0.10)\mu_B$ per Cu atom at 78 K. It is instructive to compare this result with values obtained in related Cu and Ni magnetic compounds, as is done in Table III. The Cu moment in CuO falls in between those observed in $KCuF_3$ and K_2CuF_4. Theoretical calculations will be required to resolve the relative importance of covalency versus spin fluctuations in this compound.

Figure 1 shows the intensity of the magnetic peak $(\frac{1}{2}0\frac{\bar{1}}{2})$ as a function of temperature. The Néel temperature can be determined from this figure as 225±5 K, in good agreement with the specific heat measurement. It is interesting to notice that above the Néel temperature, there is a weak and broad peak around the position of the $(\frac{1}{2}0\frac{\bar{1}}{2})$ magnetic peak (Fig. 4). Comparison of the peak intensity obtained in double- and triple-axis modes of the

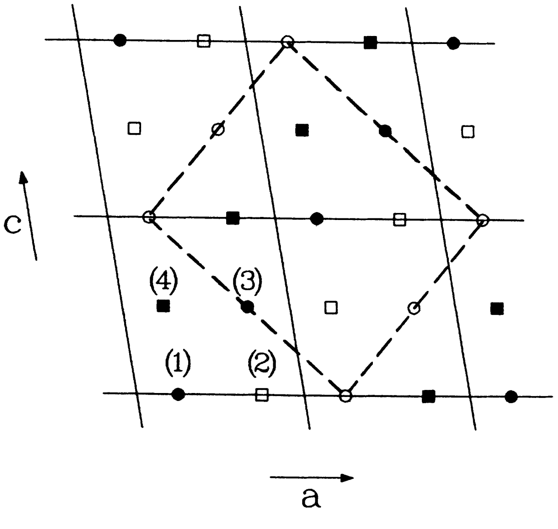

FIG. 3. The magnetic structure of CuO. The circles denote the Cu ions in the $(x,\frac{1}{4},z)$ plane, and the squares denote those in the $(x,\frac{3}{4},z)$ plane. The filled symbols denote the ions with spins pointing to [111] direction, while the open symbols denote the spins pointing to the opposite direction. Within each plane, the Cu^{2+} spins are arranged completely antiferromagnetically along the Cu-O-Cu chains running in $[10\bar{1}]$ direction. The dashed line illustrates a magnetic unit cell.

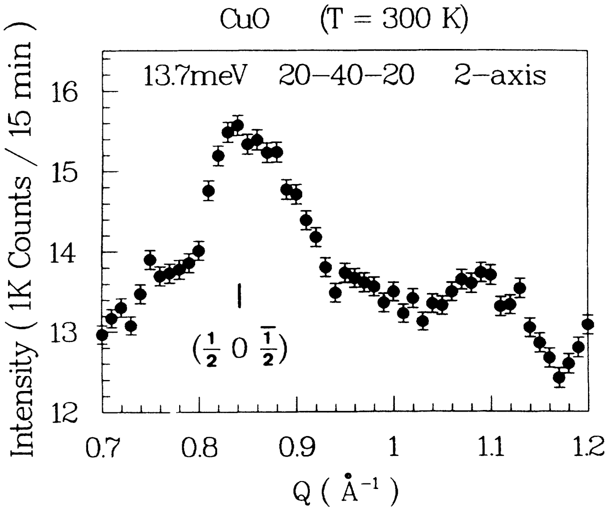

FIG. 4. The diffuse scattering around the $(\frac{1}{2}0\frac{\bar{1}}{2})$ magnetic peak position ($T=300$ K).

TABLE III. Effective magnetic moments of Cu and Ni in a few selected compounds. The compounds listed here are all antiferromagnetic except for K_2CuF_4 which is ferromagnetic.

Compound	M = Ni	M = Cu	Ref.
MO	1.81(20)	0.68(10)	13, this work
KMF_3	1.95(2)	0.48(5)	14,15
K_2MF_4	1.86(10)	1.00	16,17
La_2MO_4		0.1–0.5[a]	3–5
Full moment[b]	2.25	1.1	18

[a] The effective spin of Cu in La_2CuO_4 depends strongly on the concentration of oxygen vacancies in the crystal.

[b] The moment values listed here are for ions in crystal fields with tetragonal symmetry, without considering the covalency effect or the spin fluctuations. Their departures from the free ion values are due to the electron spin-orbit interaction which couples the ground state to other orbital states (Ref. 18).

spectrometer indicates that the scattering is mostly elastic. The peak persists up to about 400 °C, the limit of our furnace, with little change in amplitude. Such a behavior is in clear contrast to the magnetic diffuse scattering found in La_2CuO_4 (Ref. 6), where the magnetic scattering above the Néel temperature is mostly inelastic originated from the strong correlation among Cu^{2+} moments within CuO_2 planes. It is conceivable that the peak observed in CuO is also due to diffuse magnetic scattering but originating from one-dimensional correlations along the Cu-O-Cu chains. Such a picture would also be consistent with the broad maximum in magnetic susceptibility. Initial measurements with polarized neutrons have too poor a signal-to-noise ratio to determine whether or not the diffuse scattering is actually magnetic; further experimental investigation is required to confirm this speculation.

Note added in proof. During the course of analyzing single crystal measurements, we came to realize that our original conclusion concerning the spin direction was in error. In general, experimentally measured intensities can be too large due to multiple scattering or contamination from impurities, but they should never be significantly smaller than calculated values. Comparison of the calculated and measured intensities for the $(\frac{1}{2}1\bar{\frac{1}{2}})$ peak them clearly rules out the [111] spin direction. With the spin in the [010] direction, the discrepancy for the $(\frac{1}{2}0\frac{3}{2})$ reflection could be due to the magnetic form factors. Thus, we conclude that the spin is in the [010] direction.

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