Neutron-scattering study of the transition from antiferromagnetic to weak ferromagnetic order in La_2CuO_4

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(Received 25 April 1988)

Neutron-scattering studies provide direct evidence for a field-driven magnetic transition which originates from the canting of spins out of the CuO_2 planes: At the transition between antiferro- and ferromagnetic ordering of the canted component of the spins in the layers, the (100) Bragg peak vanishes while the (201) peak appears. Detailed measurements and analysis suggest that the phase transition can be described by the mean-field theory of Thio *et al.* only close to the Néel temperature.

I. INTRODUCTION

The discovery[1] of high-temperature superconductivity in copper oxides has rekindled interest in their magnetic as well as transport properties. It is now known that the phase diagrams of $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{6+\delta}$ contain regions, at very small x or δ, with three-dimensional (3D) antiferromagnetic long-range order.[2] There is growing evidence,[3] also, for a region at larger x or δ of the spin-glass phase predicted by Aharony *et al.*[4] That the 3D antiferromagnetism is destroyed in this way by a very low density of holes is evidence that the excess holes are strongly coupled to the Cu^{2+} spins. In addition to the static spin correlations, in these regions with low hole density, dynamic, highly inelastic, 2D spin fluctuations have been observed[5] even in the high-T_c superconducting phase, at least for $La_{2-x}Sr_xCuO_4$. Although the length scale ξ_{2D} of these correlations is drastically reduced by the addition of holes to the CuO_2 layers, with increasing x (δ), the moment per Cu ion participating in the spin correlations remains constant. Any theory of the superconductivity must therefore take into account that the system is composed of a concentrated, rapidly fluctuating spin system strongly coupled to the carriers. This is most straightforward if, as in a variety of models, the magnetism itself provides the pairing interaction necessary for superconductivity.

When it was first discovered that ξ_{2D} for the instantaneous 2D correlations in the paramagnetic phase of stoichiometric La_2CuO_4 is ~ 200 Å at 300 K, it appeared that such a large length scale required a new magnetic state, perhaps the resonating-valence-bond (RVB) state of Anderson.[6] However, Chakravarty *et al.*[7] have demonstrated that the size of ξ_{2D} is just that expected for the 2D, spin-$\frac{1}{2}$ Heisenberg model with a Néel ground state at $T=0$ K. Indeed, were it not for quantum renormalization effects, the correlation length would be macroscopic at room temperature because of the very large nearest-neighbor Cu-Cu exchange,[8] $J_{NN}\sim 1300$ K. This high-energy scale is a necessary ingredient in magnetic models for superconductivity.

The largest deviations from the 2D $S=\frac{1}{2}$ Heisenberg Hamiltonian for La_2CuO_4 are antisymmetric exchange terms generated by the small rotation of the CuO_6 octahedra in the orthorhombic phase. Recent magnetization measurements[9,10] reveal that in the Néel state the Cu^{2+} spins do not lie exactly in the CuO_2 layers as previously believed, but are canted out of the layer because of the antisymmetry exchange. The small canting angle, $\theta=0.003$ rad, is a measure of the accuracy with which the system is described by a simple Heisenberg Hamiltonian. The antisymmetric exchange provides a coupling between the uniform magnetic moment in the **b** direction (tetragonal c), normal to the CuO_2 layers, and the staggered moment in the **c** direction, in the layers. Thio *et al.*[9] constructed a model based on the 2D susceptibility of Chakravarty *et al.*[7] together with the antisymmetric exchange. Treating the interlayer coupling in mean-field theory, they hence could account quantitatively for the large ferromagnetic peak in the susceptibility at the Néel temperature. The antisymmetric exchange is also the origin of the gap for excitation of in-plane spin waves. This gap,[11] ~ 1 meV, at first seemed surprisingly large since the symmetry is so close to tetragonal. However, the value for the antisymmetric exchange deduced from the measured gap is in good agreement with that determined both from the canting angle and from the singular part of the susceptibility at T_N.

The antisymmetric exchange is expected to be important in the disordered state as well. The additional holes created by increasing x (δ) are expected to create local uniform moments. Through the antisymmetric exchange these give rise to a random staggered field. The random field may be important in the spin-glass phase and even, as recently suggested,[12] in the superconductivity. For all these reasons a thorough characterization of the antisymmetric exchange and its consequences is important.

The canting of the spins was first revealed[9,10] by an increase of the magnetic moment at a critical field H_c because of an assumed transition from antiferro- to ferromagnetic ordering of the canted component of the spins in the layers. It was immediately apparent that this transition required dramatic changes in the antiferromagnetic structure. We report here elastic neutron scattering experiments which confirm those predicted changes and therefore provide strong support for the model of Refs. 9 and 10. The measurements of H_c as a function of T are in agreement with those from magnetization and magnetoresistance, but are more precise, and therefore provide a more stringent test of the mean-field description of the phase boundary.

II. THEORETICAL BACKGROUND

Figure 1(a) shows the structure and spin arrangement in the ordered state of La_2CuO_4. The rotation of the CuO_6 octahedra is indicated by open arrows in Fig. 1(a) and is illustrated (greatly exaggerated) in a projection along **a** in Fig. 1(b). Also shown is the canting of the spins in the zero-field state in which, because of the interlayer antiferromagnetic exchange, alternate layers cant in opposite directions.

The spin configuration of a single CuO_2 layer may be understood by considering the spin Hamiltonian for nearest-neighbor interactions:

$$H=\sum_{\langle NN\rangle} \mathbf{S}_i \cdot \overleftrightarrow{J}_{NN} \cdot \mathbf{S}_{i+\delta} , \tag{1}$$

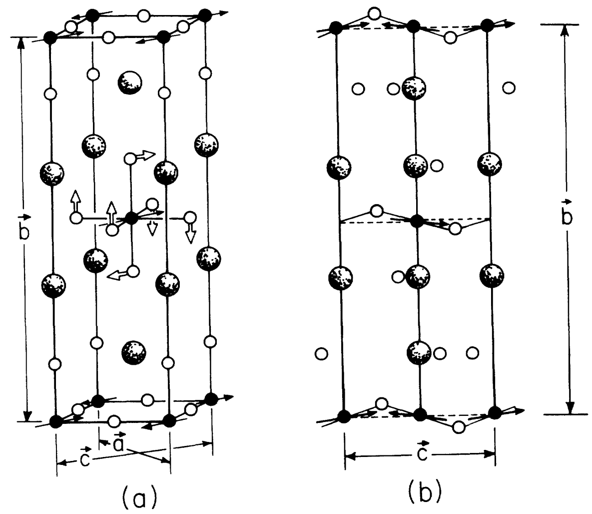

FIG. 1. Structure and spin configuration in the long-range-ordered magnetic state of La_2CuO_4. O^{2-} ions are open circles, Cu^{2+} are closed, and La^{3+} are shaded. In (a) the rotation in the orthorhombic phase is indicated by open arrows on the oxygen ions surrounding the Cu^{2+} at $(0,\frac{1}{2},\frac{1}{2})$. In (b), which is a projection along **a**, the rotation and the canting of the spins are exaggerated for clarity.

where

$$\overleftrightarrow{J}_{NN}=\begin{pmatrix} J^{aa} & 0 & 0 \\ 0 & J^{bb} & J^{bc} \\ 0 & -J^{bc} & J^{cc} \end{pmatrix} .$$

Because of the antisymmetric term,[13,14] the spins are canted by an angle θ in the **b** direction away from **c**; θ is given by $\theta = J^{bc}/2J_{NN}$ where $J_{NN}=\frac{1}{3}(J^{aa}+J^{bb}+J^{cc})$. The spins lie in the a-c plane because $|J^{bb}|$ is the smallest of the diagonal terms in $\overleftrightarrow{J}_{NN}$.

The antiferromagnetic interlayer exchange $J_\perp$ causes successive a-c layers to cant alternatively in the **b** direction at zero field, but above H_c the canting becomes uniform. Because $J_\perp$ is small and ξ_{2D} is large near T_N where the phase transition is second order, Thio *et al.* treated the transition in mean-field theory. They defined staggered moments $M_i^{\dagger}$ and fields $\mathbf{h}_i^{\dagger}$ for the individual layers ($i=1,2$) of canted spins. In the absence of J^{bc}, one would set $\mathbf{M}_i^{\dagger}=\chi_{2D}^{\dagger}\mathbf{h}_i^{\dagger}+O(h_i^{\dagger})^3$, where $\chi_{2D}^{\dagger}$ is the staggered susceptibility of the 2D, spin-$\frac{1}{2}$ Heisenberg model, $\chi_{2D}^{\dagger}=(\xi_{2D}/a)^2/kT$, and a is the Cu-Cu distance. From the $\mathbf{M}_i^{\dagger}$ and $\mathbf{h}_i^{\dagger}$ they generated symmetric and antisymmetric combinations which obey the mean-field equations

$$\mathbf{h}_{\pm}^{\dagger}=\mathbf{h}_1^{\dagger}\pm\mathbf{h}_2^{\dagger}=(\chi_{2D}^{-1}\pm J_\perp)\mathbf{M}_{\pm}^{\dagger}+A[(|\mathbf{M}_{+}^{\dagger}|^2+|\mathbf{M}_{-}^{\dagger}|^2)\mathbf{M}_{\pm}^{\dagger}+2(\mathbf{M}_{+}^{\dagger}\cdot\mathbf{M}_{-}^{\dagger})\mathbf{M}_{\mp}^{\dagger}] , \tag{2}$$

where $\mathbf{M}_{\pm}^{\dagger}=\mathbf{M}_1^{\dagger}\pm\mathbf{M}_2^{\dagger}$, and A is weakly T dependent. Differentiating Eq. (2) with respect to $\mathbf{M}_{\pm}^{\dagger}$ gives the symmetric and antisymmetric staggered susceptibilities $(\chi_{\pm}^{\dagger})^{-1}$. Below T_N, where the nonlinear terms are important, setting $\mathbf{h}_i^{\dagger}=0$ and $\mathbf{M}_{+}^{\dagger}=0$ in Eq. (2) gives $A|\mathbf{M}_{-}^{\dagger}|^2=[J_\perp-(\chi_{2D}^{\dagger})^{-1}]$, where

$$(\chi_{\pm}^{\dagger})^{-1}=\begin{cases}(\chi_{2D}^{\dagger})^{-1}\pm J_\perp+3[J_\perp-(\chi_{2D}^{\dagger})^{-1}], & T\le T_N , \\ (\chi_{2D}^{\dagger})^{-1}\pm J_\perp, & T\ge T_N .\end{cases} \tag{3}$$

Thus, the three-dimensional antisymmetric staggered susceptibility ($\chi^{\dagger}_{-}$) diverges at the Néel temperature given by $J_{\perp}\chi^{\dagger}_{2D}=1$.

For nonzero H but $h^{\dagger}_{-}=0$, Eq. (2) yields

$$A|M^{\dagger}_{-}|^2=J_{\perp}-(\chi^{\dagger}_{2D})^{-1}-3A|M^{\dagger}_{+}|^2$$
$$=A[|M^{\dagger}_{-}(H=0)|^2-3|M^{\dagger}_{+}|^2] .$$

Because of J^{bc}, an external field H in the **b** direction generates a staggered field in the **c** direction $h^{\dagger}_{+}=2J^{bc}\chi_0 H$ which yields a moment $M^{\dagger}_{+}=2J^{bc}\chi_0 H\chi^{\dagger}_{+}$ where χ_0 is the uniform susceptibility of the 2D system. Therefore

$$|M^{\dagger}_{-}(H)|^2=3|2J^{bc}\chi_0\chi^{\dagger}_{+}|^2(H_c^2-H^2) . \qquad (4)$$

Equation (4) should hold only when the transition is continuous. At high fields, that is, low T, the fluctuations in $M^{\dagger}_{+}$ are expected to make transition first order at a tricritical point.[15]

We turn next to the consequences for neutron scattering of this antiferromagnetic-to-ferromagnetic transition. The uniform moment ($\sim 10^{-3}\mu_B$) is much too small to be directly detected by neutron scattering. However, the transition in the ordering of the canted layers is accomplished by a fundamental change in the magnetic structure that is easily observed. The Bragg scattering cross section is given by

$$\frac{\partial^2\sigma}{\partial\Omega_f\partial E_f}=\sum_{\alpha}(1-\hat{G}_\alpha^2)\frac{1}{N}\langle S^\alpha(\mathbf{G},t)\rangle^2\delta(\omega) , \qquad (5)$$

where G is a magnetic reciprocal-lattice vector, and the magnetic structure factor is

$$\mathbf{S}(\mathbf{Q},t)=\sum_{\mathbf{R}}e^{i\mathbf{Q}\cdot\mathbf{R}}\mathbf{S}(\mathbf{R},t) . \qquad (6)$$

It is because the structure factor depends on the spin directions that we can detect the transition driven by the very small uniform moment in each layer. The spin configuration in Fig. 1 is for $H=0$; according to our prediction, at fields above H_c the spins in the middle layer should be rotated by 180°. That is, the spins in the orthorhombic unit cell at $(0,0,0)(\mathbf{S}\|\hat{c})$ and $(\frac{1}{2},0,\frac{1}{2})(\|-\hat{c})$ are unchanged at H_c but those at $(0,\frac{1}{2},\frac{1}{2})(\|\hat{c})$ and $(\frac{1}{2},\frac{1}{2},0)(\|-\hat{c})$ for $H<H_c$ change sign above H_c.

Whether the interlayer moment is uniform ($M^{\dagger}_{+}$) or staggered ($M^{\dagger}_{-}$) is determined by the relative directions of the nearest-interlayer-neighbor spins, those at $(\frac{1}{2},0,\frac{1}{2})$ and $(\frac{1}{2},\frac{1}{2},0)$, for instance. The in-plane component of the structure factor may be written

$$S^c=(M_1^{\dagger})^c(1-e^{i\pi(h+l)})+(M_2^{\dagger})^c e^{i\pi k}(e^{i\pi l}-e^{i\pi h}) , \qquad (7)$$

where $|(M_1^{\dagger})^c|=|(M_2^{\dagger})^c|$ but the relative signs change at H_c. Thus, for scattering with wave vector $h\mathbf{a}^*+l\mathbf{c}^*$ the h odd, l even Bragg intensity is proportional to $|(M_1^{\dagger})^c-(M_2^{\dagger})^c|^2$ which is $|M^{\dagger}_{-}(H)|^2$ to one part in $\sim 10^3$. Similarly, the h even, l odd intensity is proportional to $|M^{\dagger}_{+}(H)|^2$. Consequently, Eq. (4) gives the theoretical dependence of the Bragg intensity on H and predicts that H_c^2 is proportional to the zero-field Bragg intensity, $[M^{\dagger}_{-}(H=0)]^2$ divided by $(\chi^{\dagger}_{+})^2$.

III. RESULTS

The experiments were carried out at the Brookhaven High Flux Beam Reactor using the H4M triple-axis spectrometer. The neutron energy was fixed at 14.7 meV and collimators were 20′-40′-20′-80′. The La_2CuO_4 crystal, the same one studied in Ref. 9, was mounted in a ^{4}He cryostat with **b** vertical, along the field direction of a split-coil superconducting magnet ($H\le 6$ T). The scattering was measured in the $\mathbf{a}^*$-$\mathbf{c}^*$ plane. In this plane the nuclear structure factor which, in contrast with the magnetic one, contains equal phase factors at all sites, vanishes for $h+l$ odd.

Figure 2 shows the intensity of the (100) and (201) Bragg peaks, proportional to $|M^{\dagger}_{-}(H)|^2$ and $|M^{\dagger}_{+}(H)|^2$, respectively, as functions of magnetic field at 80 K. At about 4.8 T the peak with h odd and l even disappears and that with h even and l odd appears. There can, therefore, be little doubt that the canted spin arrangement depicted in Fig. 1(b) is accurate. The hysteresis obvious in Fig. 2 was also seen in measurements of magnetization $M(H)$ and magnetoresistance $R(H)$ at low temperature where the transition is expected to be first order.

Figure 3 shows the (100) intensity versus the square of the magnetic field for several temperatures. It is apparent that the linear dependence on H^2 predicted by Eq. (4) is a good description of the data only for the two temperatures within 15 K of $T_N=234$ K.

From data like those in Figs. 2 and 3 we measured H_c for $T<230$ K. However, closer to T_N, H_c varies too rapidly with T for an accurate determination in this way. We therefore determined this part of the phase boundary by

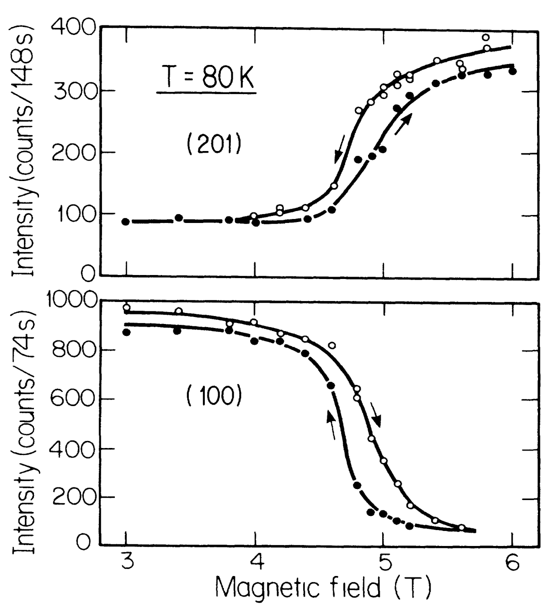

FIG. 2. Magnetic field dependence of the structure factor. The Bragg intensity at (100) decreases with H (lower panel), and that at (201) increases with H (upper panel) because of the transition from antiferromagnetic ordering of the canted component of the spins, depicted in Fig. 1, to ferromagnetic ordering.

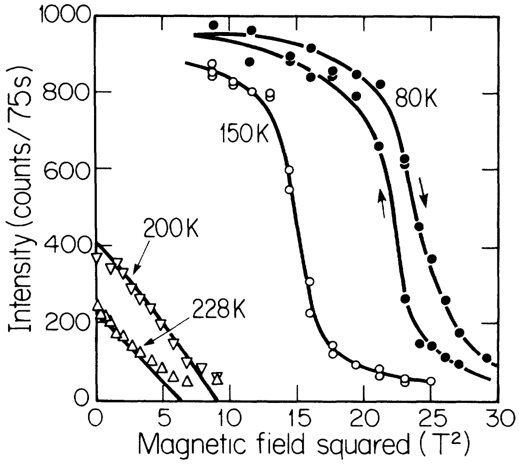

FIG. 3. Field dependence of the (100) Bragg peak at various temperatures. The linear dependence on H^2 predicted by Eq. (4) is observed only for the two temperatures within 15 K of the Néel temperature. Even at 80 and 5 K (not shown) the transition is broad, despite the evident hysteresis indicating that it is first order.

measuring the (100) intensity versus T at fixed magnetic field. Figure 4 shows the resulting phase boundary between the antiferro- and ferromagnetic arrangement of the canted spins. Also shown are measurements of H_c from the magnetization $M(H)$ and magnetoresistance $R(H)$ for the same sample (Ref. 9). The Bragg intensity in Ref. 9 was for a different, but identically grown crystal, but the data agree well with those presented in Fig. 4.

We have plotted H_c^2 and $|M_-^{\dagger}(H=0)|^2$ divided by $(\chi_+^{\ddagger})^2$ in Fig. 4, for comparison with the prediction of Eq. (4); $\chi_+^{\ddagger}$ was computed using Eq. (3) with $\xi_{2D}(T)$ from

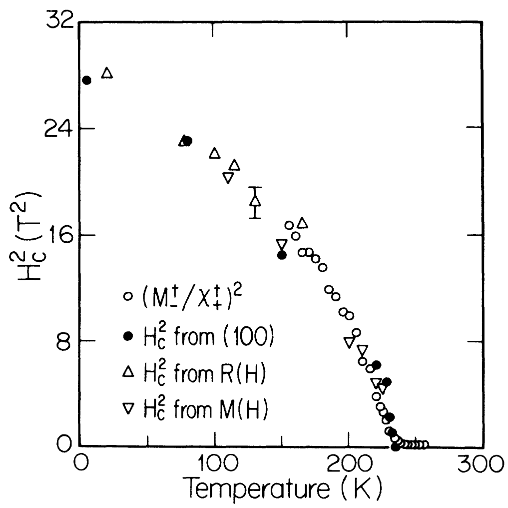

FIG. 4. Boundary between antiferro- and ferromagnetic ordering of the canted components of the Cu^{2+} spins. Values of H_c obtained from the (100) Bragg peak in this experiment are in good agreement with those from magnetoresistance $R(H)$ and magnetization $M(H)$ in Ref. 9. $[M_-^{\dagger}(H=0)/\chi_+^{\ddagger}]^2$ is plotted in arbitrary units and normalized to the other data at ~205 K.

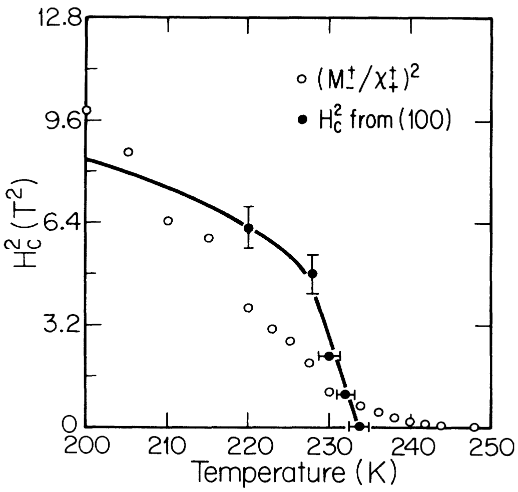

FIG. 5. Comparison of H_c^2, measured as described in the text, with $[M_-^{\dagger}(H=0)/\chi_+^{\ddagger}]^2$. The latter is in arbitrary units. If the two quantities were normalized at 220 K instead of ~205 K they would coincide within ~15 K of T_N.

Chakravarty *et al.*[7] Over this wide temperature range, with the quantities normalized at about 200 K, the agreement seems quite reasonable. However, when one examines the region close to T_N, as in Fig. 5, one sees that the critical field rises much more steeply with decreasing T than does the Bragg peak intensity divided by $\chi_+^{\ddagger}$. One could, alternatively, normalize the quantities at 220 K which would give agreement with Eq. (4) within ~15 K of T_N but not lower T.

IV. DISCUSSION AND CONCLUSIONS

Figure 2 provides dramatic confirmation for the predicted change in the magnetic structure resulting from the coupling between the 2D canting of the spins. This in turn verifies the importance of the antisymmetric exchange in La_2CuO_4 as inferred previously from magnetization measurements.[9,10] It was shown in Ref. 9 that mean-field theory gives a quantitative explanation of the ferromagnetic peak in the susceptibility at T_N. However, whereas some of the behavior predicted by the theory is observed in the present experiment, Figs. 3 and 5 suggest discrepancies.

The most straightforward interpretation of these results is that the mean-field theory holds only within ~15 K of T_N. In this region $|M_-^{\dagger}(H)|^2$ is proportional to $H_c^2-H^2$ and $[M_-^{\dagger}(H=0)/\chi_+^{\ddagger}]^2$ is proportional to H_c^2. This is not in conflict with the susceptibility measurements since the low-temperature part of the ferromagnetic peak has a width of only ~10 K. In retrospect, this narrow range of mean-field behavior is not surprising. In a system like La_2CuO_4, which is so well described by the Heisenberg model, spin-wave excitations are expected to alter significantly the shape of the low-temperature phase boundary.

It would be interesting to determine precisely the location of the tricritical point. However, examination of Figs. 2 and 3 shows that this is impossible for the crystal studied here. Even at 80 and 5 K (not shown), where the hysteresis is appreciable and the transition appears therefore to be first order, the transition is nonetheless unexpectedly broad ($\sim$0.4 T). The origin of this broadening may be the random staggered field induced by the holes. Consequently, it is not possible to tell whether the transition, at 150 K for example, is first order but broadened by the random fields or second order. The random field probably contributes to the rounding of the transition seen in the $|M_{-}^{\dagger}(H=0,T)|^2$ data, especially in Fig. 5. This may be an additional source of the disparity between the latter and $H_c^2(T)$.

ACKNOWLEDGMENTS

We acknowledge helpful discussions with A. Aharony. This work was supported by the U.S.-Japan Cooperative Neutron Scattering Program, and a Grant In Aid for Scientific Research from the Japanese Ministry of Education, Science and Culture. The work at MIT was supported by the National Science Foundation under Grants No. DMR85-01856, No. DMR84-18718, and No. DMR84-15336. Research at Brookhaven is supported by the Division of Materials Science, U.S. Department of Energy under Contract No. DE-AC02-CH00016.

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