

Structural Phase Transition in KHCO_3

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The structural phase transition of KHCO_3 has been studied using three-dimensional data collected both below and above the transition point. Above 318 K, the crystal structure changes from the room temperature phase (monoclinic space group $P2_1/a$) to a high temperature phase (monoclinic space group $C2/m$), both containing four formula units. The cell dimensions are $a = 15.195(1) \text{ \AA}$, $b = 5.640(1) \text{ \AA}$, $c = 3.734(1) \text{ \AA}$, and $\beta = 104.86(1)^\circ$, and $v = 309.28 \text{ \AA}^3$ (at 353 K). The structure is refined by the full-matrix least-squares method and final R -factor is 0.023. From the hydrogen atoms revealed in the difference Fourier map, it is concluded that the phase transition is ascribed to the order–disorder of the $(\text{HCO}_3)_2$ dimer. © 1990 Academic Press, Inc.

1. Introduction

The hydrogen bonding was first recognized by Zachariassen in 1933 (1) by solving the crystal structure of sodium hydrogen carbonate NaHCO_3 . The structure is composed of hydrogen bond networks of HCO_3 ions. The title compound belongs to this family and also contains the hydrogen bonding. However, it utilizes a different bonding scheme and contains $(\text{HCO}_3)_2$ dimers instead of HCO_3 chains (2, 3). The dynamical transfer of hydrogen atoms in such a hydrogen bond dimer attracts wide interest; the transfer is simulated by a motion of light atoms in a symmetric or asymmetric double minimum potential (4). Detailed neutron diffraction study done by Thomas *et al.* (5) revealed two sites for the hydrogen atom. The result suggests a disorder of the $(\text{HCO}_3)_2$ dimers in the room temperature phase. Recently, by means of ultrasonic velocity measurement, Haussühl (6) reported that KHCO_3 undergoes a phase transition at 318 K.

In order to make clear the nature of the phase transition and determine the structure of this newly found high temperature form, we have made detailed X-ray scattering experiments of KHCO_3 crystals both above and below the transition point.

2. Experimental

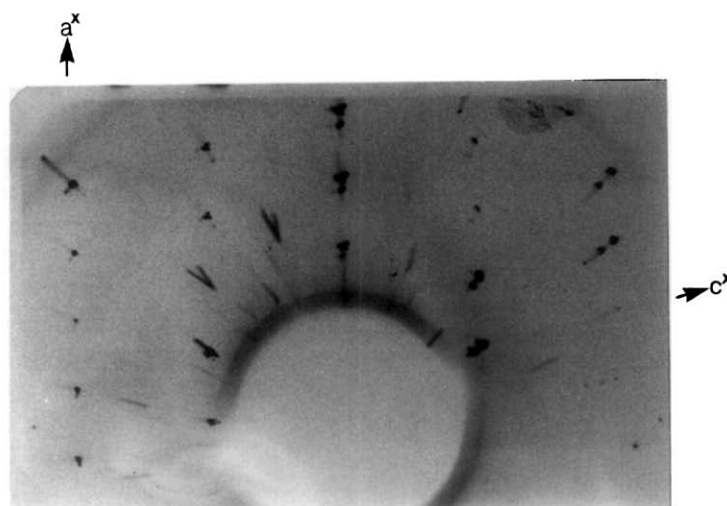
Potassium hydrogen carbonate crystals were prepared from a slightly warm concentrated water solution of analytical grade KHCO_3 . Colorless prismatic crystals, elongated along the c -axis, were generally formed on cooling. Preliminary data of the structure were gathered by the photographic method; precession photographs were taken at several temperatures between 290 and 360 K. As a heating device, a small electric furnace was mounted on a goniometer head. The temperature of the sample was kept constant within 3 K during the exposure.

The crystal structure of KHCO_3 is reported first by Nitta *et al.* (2) and later more

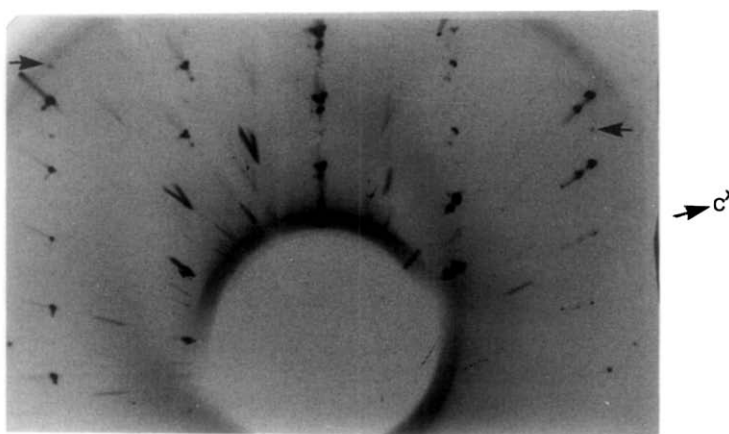
detailed structure data, by Thomas *et al.* (3). The structure belongs to the monoclinic space group $P2_1/a$. Figure 1 shows the first layer precession photographs taken along the b -axis, (a) at room temperature and (b) at 338 K. In Fig. 1a, weak spots are observed midway between the dense spots lined along the a^* -direction. In contrast, these fine spots are lacking in Fig. 1b. If the

sample is cooled to room temperature, these weak spots appear again suggesting that the transition is of the reversible type. In the zero level photograph taken along the b -axis, these weak spots are absent even at the room temperature phase because of the presence of an a -glide.

The observed extinction rules are $h = 2n + 1$ for the $h0l$ reflections (at 290 K) and h



(b) 338 K



(a) 290 K

FIG. 1. The first layer precession photographs along the unique b : axis: (a) at 295 K; (b) at 338 K. Note that the superlattice spots represented by arrows in (a) are absent in (b).

+ $k = 2n + 1$ for the hkl reflections (at 338 K). The space group expected from the former extinction rule is unique, $P2_1/a$, but the space group deduced from the latter extinction rule is not unique as is one among those of $C2$, Cm , and $C2/m$.

Detailed structural data were collected using an automatic single crystal diffractometer assembled in our laboratory. As an X-ray source a Mac Science generator "MO3C" (3 kW, max) with Mo target was used. Incident X-ray beam was monochromated by a flat graphite monochromator. The main part of the diffractometer consisted of a two-circle goniometer (Huber "424") and an off-center type Eulerian cradle (Huber "511.1"). The distance between the X-ray target and the monochromator was 106 mm, and the distances between the monochromator and the crystal and the crystal to the cross slit screen were 205 and 275 mm, respectively. The aperture of the receiving slit used was 8×8 mm.

A crystal of KHCO_3 was ground into a sphere (diameter 0.48 mm) and was mounted on a goniometer head. The sample was set in a controlled air stream, and the temperature was kept constant within 1 K. The unit cell parameters were derived by the least-squares method from 18 reflections within the range of $30 < 2\theta < 43$. The obtained unit cell parameters are given in Table I. From the scanning of the $5\ 2\ 0$ reflection, which disappears in the high

temperature phase, the transition temperature was estimated as 318 K.

The integrated intensities were collected by the Ω - 2θ scan method and the scan range was determined as $\nabla 2\theta = 3.0 + 1 \times \tan \theta$. The scanning rate was 2 degree per minute for the 2θ angle. Background counts were measured for 10 sec at each limit of the scan range. Intensities of the unique reflections with indices $\pm h$, $+k$, $+l$ were collected up to $2\theta = 60$. Three standard reflections $12\ 0\ 0$, $0\ 4\ 0$, and $0\ 0\ 3$ were monitored every 100 reflections. There was no significant change in the intensity of the standard reflections throughout the data collection, thereby assuring crystal and hardware stability. The data were corrected for the Lorentz, polarization, and absorption effects ($\mu = 14.9\ \text{cm}^{-1}$ and $\mu R = 0.36$). Reflections for which the intensities were less than their standard deviation were regarded as "unobserved" and were not included in subsequent calculations. The resulting numbers of "observed" reflections were 932 (at 301 K) and 470 (at 353 K).

3. Analysis of Experimental Results and Discussion

(a) Room Temperature Phase

The values of the atomic coordinates given by Thomas *et al.* (3) were used as the initial parameters. The refinement was done using the full-matrix least-squares program "RADIEL" (7), where an isotropic extinction correction was made. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma(F_o)^2 + 0.04 |F_o|^2]^{-1}$. Scattering factors used are those listed in International Tables for X-Ray Crystallography (1974) (8). The obtained R -factor $R = \sum (|F_o| - |F_c|) / \sum |F_o|$ which included the heavy atoms was 0.026, and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2}$ was 0.034.

Figure 2a shows a $[103]$ section of the Fourier synthesis which includes a $(\text{HCO}_3)_2$

TABLE I

LATTICE CONSTANTS (\AA) AND ANGLES (DEGREES) WITH e.s.d.'s OF KHCO_3 AT THREE DIFFERENT TEMPERATURES

	301 K	317 K	353 K
a	15.181(2)	15.182(2)	15.194(2)
b	5.629(1)	5.623(3)	5.640(1)
c	3.713(1)	3.722(1)	3.734(1)
$\beta = 104.64(1)$		104.72(1)	104.86(1)

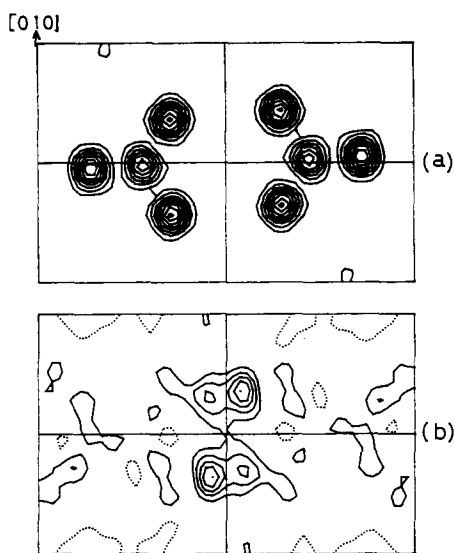


FIG. 2. Fourier map (a) and difference Fourier maps (b) in the (103) plane of KHCO_3 at the room temperature phase (301 K): Contours are drawn at intervals 1 eA^{-3} (a) and 0.1 eA^{-3} (b); solid lines indicate electron excess, and dashed lines, electron deficiency.

dimer. Hydrogen atoms linking two CO_3 molecules are well reproduced in the difference Fourier map, Fig. 2b. This map, further, reveals two asymmetric peaks for a hydrogen atom in the relevant O.H–O hydrogen bond. This asymmetric peak is already reported in the recent neutron diffraction study by Thomas *et al.* (5). The final R -factor of the refinement was $R = 0.0221$ and $R_w = 0.0279$, where the contribution of the hydrogen atom at the dominant site is included, but the effect of the partial disorder of the heavy atoms was not taken into account.¹

¹ See NAPS document No. 07466 for 29 pages of supplementary material. Order from ASIS/NAPS. Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance \$4.00 for microfiche copy or photocopy, \$7.75 up to 20 pages plus \$.30 for each additional page. All orders must be prepaid. Institutions and Organizations may order by purchase order. However, there is a billing and handling charge for this service of \$15. Foreign order add \$4.50 for postage and handling, for the first 20 pages,

A schematic description of the room temperature phase is given in Fig. 3; note that the long principal axis of the $(\text{HCO}_3)_2$ dimers is tilted in anti-phase at the center and the corner sites of the a – b plane. The potassium atoms which are connected to the oxygen atoms are also shifted alternately along b -axis. The positional and thermal parameters are in fair agreement with those reported by Thomas *et al.* (3) and not reproduced here.

(b) High Temperature Phase

The coordinates of atoms refined in the room temperature phase were used as the initial parameters. The three space groups $C2$, Cm and $C2/m$, which were derived from the observed extinction rule, were examined in the least-squares refinement. The calculation offered similar structure for the three space groups which is a slight modification of the room temperature phase. R -factors obtained for the three space groups $C2$, Cm and $C2/m$ were 0.0289, and 0.0284, and 0.0290 with parameters 46, 54, and 00. Only the last one, $C2/m$, which conserves the inversion symmetry of the room temperature structure, gave sufficient conversion results.

Two structural models were examined for this space group: First, the “displacive-type model,” where the symmetry of the dimer actually changes to $2/m$. Second, the “order–disorder model,” where the symmetry of the dimer does not change and the structure is represented by a superposition of two states having symmetry 1. In the first model, the atom O-3 is equivalent to O-2; the number of heavy atoms to be refined is reduced to four. The obtained R -factor is $R = 0.029$ and $R_w = 0.0404$ for the displacive-type model, and $R = 0.0275$ and $R_w = 0.0369$ for the order–disorder model, and the relevant number of the parameters is 29

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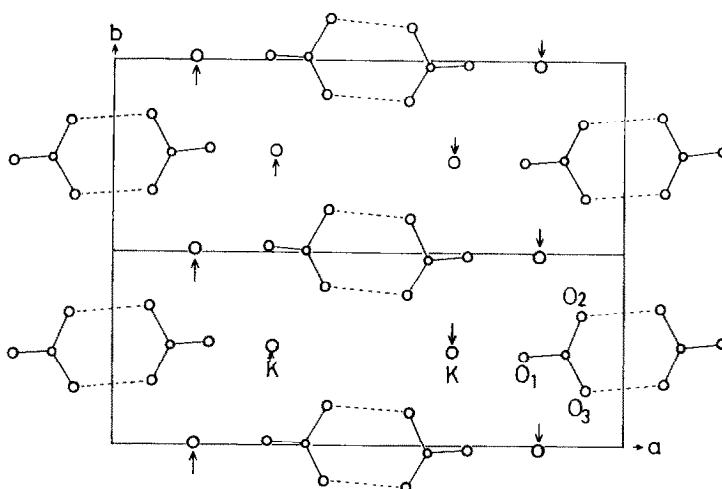


FIG. 3. A schematic illustration of the structure of KHCO_3 in the room temperature phase: (a) projection along c -axis; (b) projection along b -axis. The arrows represent displacement from the symmetrical positions occupied in the high temperature phase, see Fig. 5. The hydrogen bonds are represented by dotted lines.

and 47, respectively. According to the significance test program by Hamilton (9), the R_w factor ratio suggests that the displacive-type model is rejected at the significance level of 0.005.

The difference Fourier maps synthesized by the two models reveal the hydrogen atoms but show a strange feature (see Figs. 4b and 4c). The map synthesized by the order-disorder model in Fig. 4b shows a "single peak", whereas the map synthesized by the "displacive model" in Fig. 4c shows symmetric "double peaks."

In order to resolve this inconsistency, we have made a simple model calculation: The hydrogen atom was assumed to be in disorder and set in the general position expected from the neutron diffraction data (5). A hypothetical diffraction data set was created using the hydrogen atom and the heavy atoms which were refined by the least-squares procedure. The difference Fourier map was then synthesized by subtracting the parts due to the heavy atoms. The maps obtained by this simulation are given in Figs. 4d and 4e. It is clear that the order-

disorder model reproduces the observed results. The above inconsistency may be attributed to the fact that the gravity center of the oxygen atom refined without the hydrogen atom is shifted a little in the direction of the hydrogen atom.

Consequently, the order-disorder model was judged as adequate. The final R -factor which included the hydrogen atom was $R = 0.0230$ and $R_w = 0.0323$.¹ Figure 5 shows the structure of the high temperature phase. The positional and thermal parameters are given in Table II. Relevant bond lengths and angles are listed in Table III. Due to the difficulty in refining the parameters in disordered structure, the positional parameters have abnormally large e.s.d.'s; the thermal parameters also have large values. Finally, it may be worth while to note that although the integrated intensity of the superlattice reflections (indices $h + k = 2n + 1$) drops about two orders of magnitude above 318 K, and is below the standard deviation, these reflections do not disappear completely but fade into diffuse scattering. The diffuse scattering has a maximum around

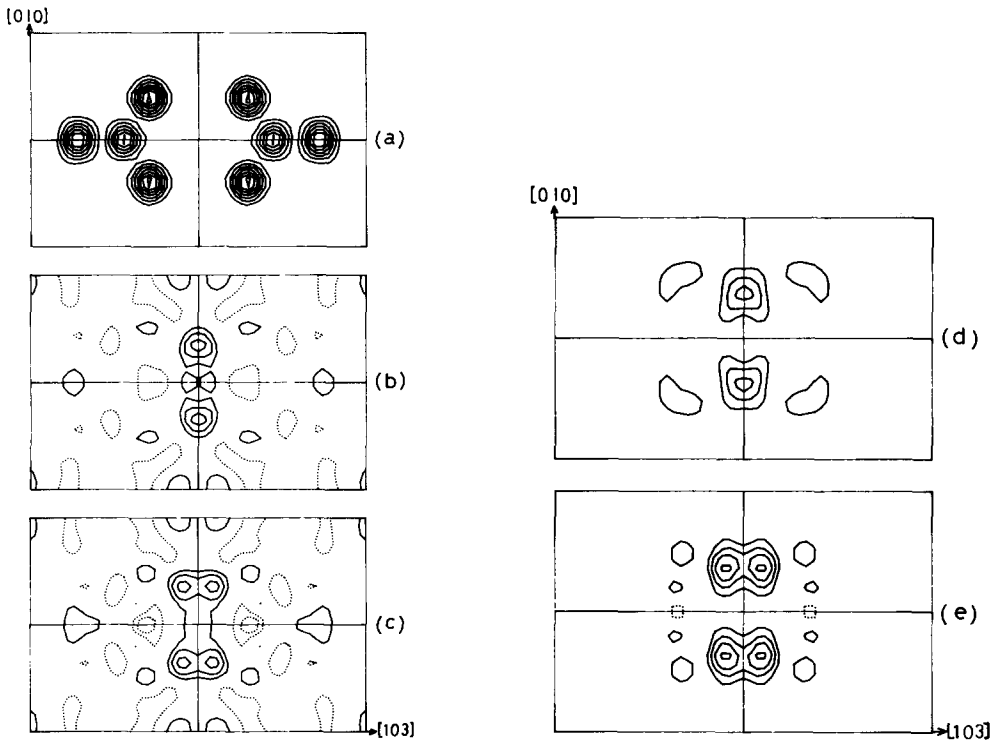


FIG. 4. Fourier map (a) and difference Fourier maps (b) and (c) in the (103) plane of the high temperature phase. Contours are drawn at intervals 1 eA^{-3} (a) and 0.1 eA^{-3} ((b), (c), (d) and (e)); solid lines indicate electron excess, and dashed lines, electron deficiency. The difference Fourier map is obtained by the "order-disorder model" (b) and by the "displacive type model" (c); (d) and (e) are the corresponding results of the simulation; see text.

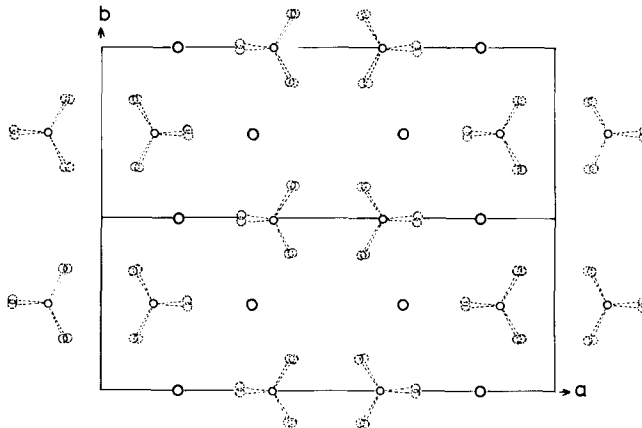


FIG. 5. A schematic illustration of the structure of KHCO_3 in the high temperature phase, projection along c -axis (the order-disorder model).

TABLE II
POSITIONAL PARAMETERS ($\times 10^4$) AND THERMAL PARAMETERS ($\times 10^3$) WITH e.s.d.'s OF KHCO_3 AT 353 K
(HIGH TEMPERATURE PHASE)

Atom	X	Y	Z	U_1	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K	1651(1)	119(155)	2956(2)	34(0)	26(13)	24(0)	2(2)	3(0)	1(1)
O ¹	1937(2)	5168(18)	944(6)	28(1)	36(22)	33(22)	4(5)	-33(5)	-3(9)
O ²	782(21)	2941(46)	-2474(97)	33(4)	27(5)	33(10)	-5(2)	-4(5)	7(4)
O ³	816(20)	6911(44)	-2947(99)	29(3)	22(4)	27(6)	-3(4)	1(3)	-1(5)
C	1193(2)	5119(62)	-1440(8)	25(1)	21(1)	23(1)	-11(6)	7(1)	-8(5)
H	323(32)	6866(90)	-4102(123)	15(13)					

Note. The form of the thermal parameter is $\exp[-2\pi^2(U_1h^2a^{*2} + \dots + 2U_{12}hk a^*b^* \cos \gamma + \dots)]$; the hydrogen atom was refined isotropically.

the superlattice point, but has a long tail along the a^* direction. The fact suggests that the local structure of the low temperature phase remains above the transition temperature.

The structural phase transition of KHCO_3 may be attributive to the symmetry change of the $(\text{HCO}_3)_2$ dimer. In a hypothetical gas phase of $(\text{HCO}_3)_2$ dimers, the hydrogen atom will be in a symmetrical double well potential (the symmetry of the dimer is $2/m$). In a real crystal, intermolecular interaction may destroy the symmetry of the potential, as shown in Fig. 3. Due to the thermal agitation, hydrogen atoms transfer from the lower potential well to the upper one, coherently. As the temperature is raised, such motion in return diminishes the asymmetry of the potential. At a certain temperature, therefore, the symmetry of the dimer will recover again to $2/m$. The experimental results suggest that the phase transition takes place at a temperature lower than the point where the symmetry of the dimer changes to $2/m$.

In a recent ultrasonic velocity measurement, Haussühl (6) reported an anomalous softening of the shear elastic constant C_{66} , near the transition temperature: the mode which propagates along the a^* direction and with polarization along b . The diffuse scattering will also suggest that a coupled

motion of the zone boundary shear acoustic mode and the orientation of the $(\text{HCO}_3)_2$ dimer (as shown by arrows in Fig. 3) has a large population of numbers and plays a

TABLE III
INTERATOMIC BOND DISTANCES (\AA) AND ANGLES (DEGREES) WITH e.s.d.'s FOR KHCO_3 AT 301 AND 353 K

	301 K	353 K
C-O-1	1.245(2)	1.247 (4) 1.245(3) ^a
C-O-2	1.278(2)	1.225 (39) 1.304(2) ^a
C-O-3	1.334(2)	1.387 (41) 1.304(2) ^a
K-O-1	3.010(1)	3.005(128)
K-O-1 ₅₄₅₁	2.932(1)	2.952(83)
K-O-1 ₅₄₅₄	2.871(1)	2.886(1)
K-O-1 ₅₄₆₄	2.696(1)	2.699(1)
K-O-2	2.743(1)	2.883(30)
K-O-2 ₅₅₆₁	2.830(1)	2.867(34)
K-O-3 ₅₄₅₁	2.886(1)	2.889(35)
K-O-3 ₅₄₆₁	2.779(1)	2.648(60)
O-1-C-O-2	123.94(1)	122.76(3)
O-2-C-O-3	118.36(1)	118.62(3)
O-3-C-O-1	117.71(1)	118.61(3)
Hydrogen bond		
O-3 . . . O-2 ₅₆₄₃	2.587(1)	2.588(29)
O-3-H	0.929(26)	0.762(52)
H . . . O-2 ₅₆₄₃	1.662(26)	1.835(43)
O-3-H . . . O-2 ₅₆₄₃	173.87(2.50)	169.38(5.03)
C-O 3 . . . O-2 ₅₆₄₃	116.63(10)	114.04(2.48)
C-O 2 . . . H ₅₆₄₃	122.58(90)	125.40(2.28)

Note. The first three digits of the identifying suffixes on atoms not in the asymmetric unit refer to a lattice translation; e.g., 564 implies the operation $(x, y + 1, z - 1)$; the fourth digit specifies one of the symmetry operations: 1, x, y, z ; 2, $1/2 + x, 1/2 - y, z$; 3, $-x, -y, -z$; 4, $1/2 - x, 1/2 + y, -z$.

^a Values refined by the "displacive-type model."

main part in the phase transition. Detailed measurement and analysis of the diffuse scattering will be sufficient to clarify the mechanism of the transition.

Acknowledgments

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