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A new elaboration process of the superconducting $Tl_2Ba_2Cu_1O_6$ phase with $T_c=90K$.

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We have synthesized high quality ceramic $Tl_2Ba_2Cu_1O_{6+\delta}$ (2201) samples using the high pressure, high temperature route. At high oxygen content, the structure is orthorhombic and the samples are metallic but non-superconducting. Upon lowering the oxygen content, the symmetry changes from orthorhombic to tetragonal or pseudo-tetragonal. In the latter phase, the maximum superconducting critical temperature reaches 92 K.

Optical micrographs show large 2201 grains and some traces of impurity phases like $Tl_2Ba_2O_5$, $Ba_2Cu_3O_x$ and CuO . X-ray diffraction shows only the 2201 phase. Plasma emission spectroscopy indicates that the global sample stoichiometry is $Tl:Ba:Cu=2:2:1$. This analysis proves that the high pressure route effectively prevents the thallium evaporation. HREM investigations exclude the possibility of cation vacancies. Microprobe analyses (EDAX) show no variation of the cation stoichiometry between the 2201 grains. X-ray diffraction on a superconducting single crystal yields a refined composition $Tl_{1.94}Ba_2Cu_{1.06}O_6$.

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1. Introduction

The layer compound $\text{Tl}_2\text{Ba}_2\text{Cu}_1\text{O}_6$ ("2201") exists in an orthorhombic and in a tetragonal phase. Although the structure refinements were carried out in three different space-groups ($I4/mmm$ [1], $Ccc2$ ($A2aa$) [2], $Fmmm$ [3]), the structural features of the tetragonal and orthorhombic samples (superconducting or not) were found to be very similar. The structure contains Tl_2O_2 double layers and one CuO_2 plane separated by a layer of barium atoms (see fig. 1). There is however no general agreement concerning the amount of vacancies and substitution of copper on the thallium site and the possible delocalisation of this site [1, 2, 3, 4]. For example, in the orthorhombic phase, using powder neutron diffraction, Hewat et al. [2] found in a non-superconducting compound a deficiency in thallium of about 1 in 8. Parise et al. [3] indicate for a superconducting sample ($T_c=90$ K) the stoichiometry $\text{Tl}_2\text{Ba}_2\text{Cu}_1\text{O}_{6.10}$. They found a small amount of interstitial oxygen (site O(4), see fig. 1) incorporated in the Tl_2O_2 layers, in contrast to Hewat et al. [2]. Shimakawa et al. [1] also detected this oxygen excess in superconducting and non-superconducting tetragonal samples and attribute the variation of T_c to the occupancy of this site.

In this paper, we report the synthesis and characterization of orthorhombic and tetragonal-90 K 2201 samples.

2. Sample preparation

The $\text{Tl}_2\text{Ba}_2\text{Cu}_1\text{O}_{6+\delta}$ (2201) samples were prepared using two starting powders.

Batch "A": CuO (Cerac, 99.9%) was added to $\text{Tl}_2\text{Ba}_2\text{O}_5$ (2200) precursor [5] to obtain the final stoichiometry $\text{Tl}:\text{Ba}:\text{Cu}:2:2:1$.

Batch "B": Using the same precursors ($2200+\text{CuO}$), the powders were first annealed under 1 atmosphere oxygen pressure at 700-750 °C during 3 days. The resulting product consists of a very small grains of 2201 phase and unreacted precursors.

After mixing, the powders were pressed under about 5 kbar into pellets and placed in Al_2O_3 crucibles. The orthorhombic non superconducting phase (sample TKO-930) was obtained using a heat treatment under 100 bar of O_2 at 900-930 °C during 30 minutes. The weight loss was less than 0.8 %. The tetragonal phase with $T_c=90-92$ K was sintered under 100 bar of helium (sample TM-850) or argon (sample TA2-850), respectively, at 850 °C during 12 minutes. The product was reground and the procedure was repeated twice in order to obtain homogeneous samples. In this case, the mass loss is more important, about 1.5 %. The high pressure route minimises the thallium evaporation and ensures complete reaction because of the high sintering temperature.

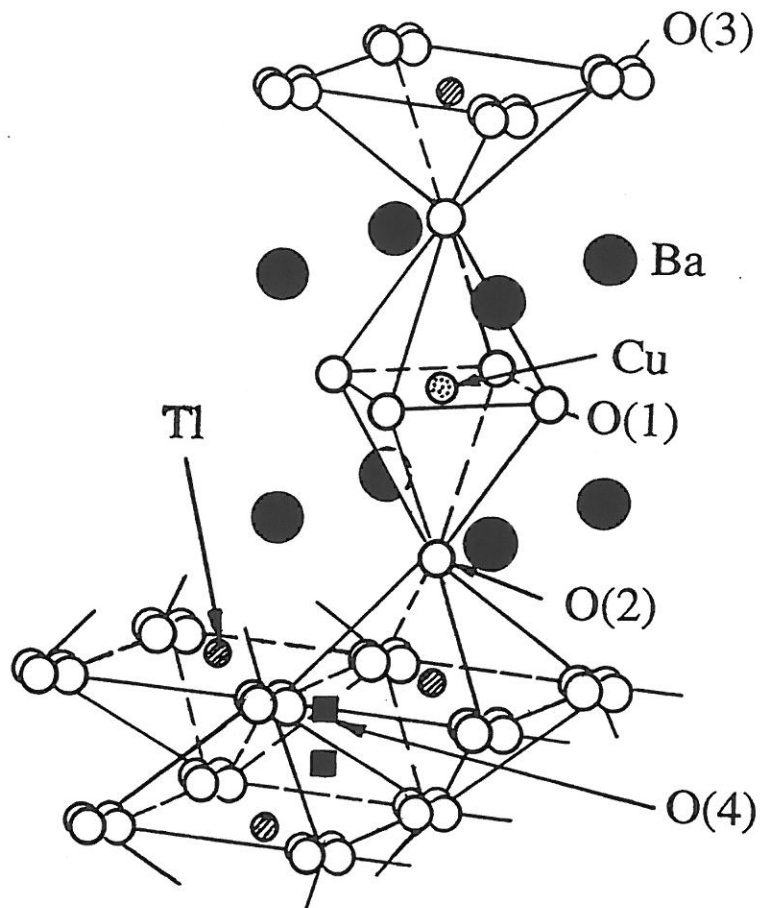


Figure 1: Structure of the tetragonal superconducting 2201 phase [1].

3. Microstructural investigations

The samples were studied at ambient temperature by X-ray powder diffraction using a Guinier camera with Cu K α radiation. Silicon was added to the powdered samples as an internal standard. The lattice parameters of the Tl₂Ba₂CuO_{6+ δ} orthorhombic and tetragonal phases were determined from least-squares fits using more than 20 lines ($10^\circ < 4\theta < 160^\circ$). The lines were indexed according to the space group *I4/mmm* for the tetragonal [1] and *Ccc2* (or *A2aa*) for the orthorhombic structure [2]. All samples are X-ray pure. Some results are listed in table I.

The global stoichiometry of the sample was determined by plasma emission spectroscopy. The result indicates for all samples (orthorhombic and tetragonal) a stoichiometry Tl:Ba:Cu=2:2:1. Microstructural investigations were performed after polishing the samples using diamond paste. The surface was examined in an optical microscope and in a scanning electron microscope (SEM, Cambridge Instruments Stereoscan 360). In the latter case, the polished samples were covered with a 6 Å thick silver layer. Energy dispersive analysis (EDAX) was performed on the M lines of thallium, L lines of barium and K lines of copper by means of a Tracor Northern system. EDAX investigations were corrected by a standard. Both for tetragonal and orthorhombic samples, we do not find any significant variation of the cation stoichiometry in the 2201 grains. However, taking into account the presence of residual impurity phases, a small difference between macroscopic and local analyses appears acceptable. The EDAX data are given in table II. Fig. 2 shows optical micrographs of the tetragonal (TM-850 and TA2-850) and an orthorhombic (TKO-930) samples. Only 2201 grains can be seen in this figure. In polarized light, some yellow traces (estimated < 5% by volume) of the 2200 precursor were detected in the samples synthesized using batch "A". The other samples (batch "B") present Ba₂Cu₃O_x impurity grains (< 0.1% by volume). Some small grains of CuO are also sometimes observed. HREM investigations exclude the possibility of cation vacancies in the 2201 orthorhombic and tetragonal structure [6, 7].

Table I:

Sample	Batch	T _c ^{onset} (K)	f%	a (Å)	b (Å)	c (Å)	Impurities
TM-850	"A"	91.1	43.9	a=b=3.8717(5)		23.225(4)	2200+CuO
TA2-850	"B"	92.1	62.8	a=b=3.8706(4)		23.224(3)	Ba ₂ Cu ₃ O _x +CuO
TKO-930	"B"	-	-	5.4467(8)	5.4911(7)	23.144(2)	Ba ₂ Cu ₃ O _x +CuO

Table II: Average of more than 25 microprobe analyses (EDAX) in the 2201 grains. The values are given in atomic %.

Sample	EDAX-local			EDAX ratio
	Tl	Ba	Cu	Tl/Cu
TM-850	39.2+/-0.8	40.2+/-1.0	20.7+/-0.6	1.89
TA2-850	38.8+/-0.6	42.3+/-0.9	19.5+/-0.6	1.99
TKO-930	40.7+/-0.4	39.2+/-0.4	20.1+/-0.8	2.02

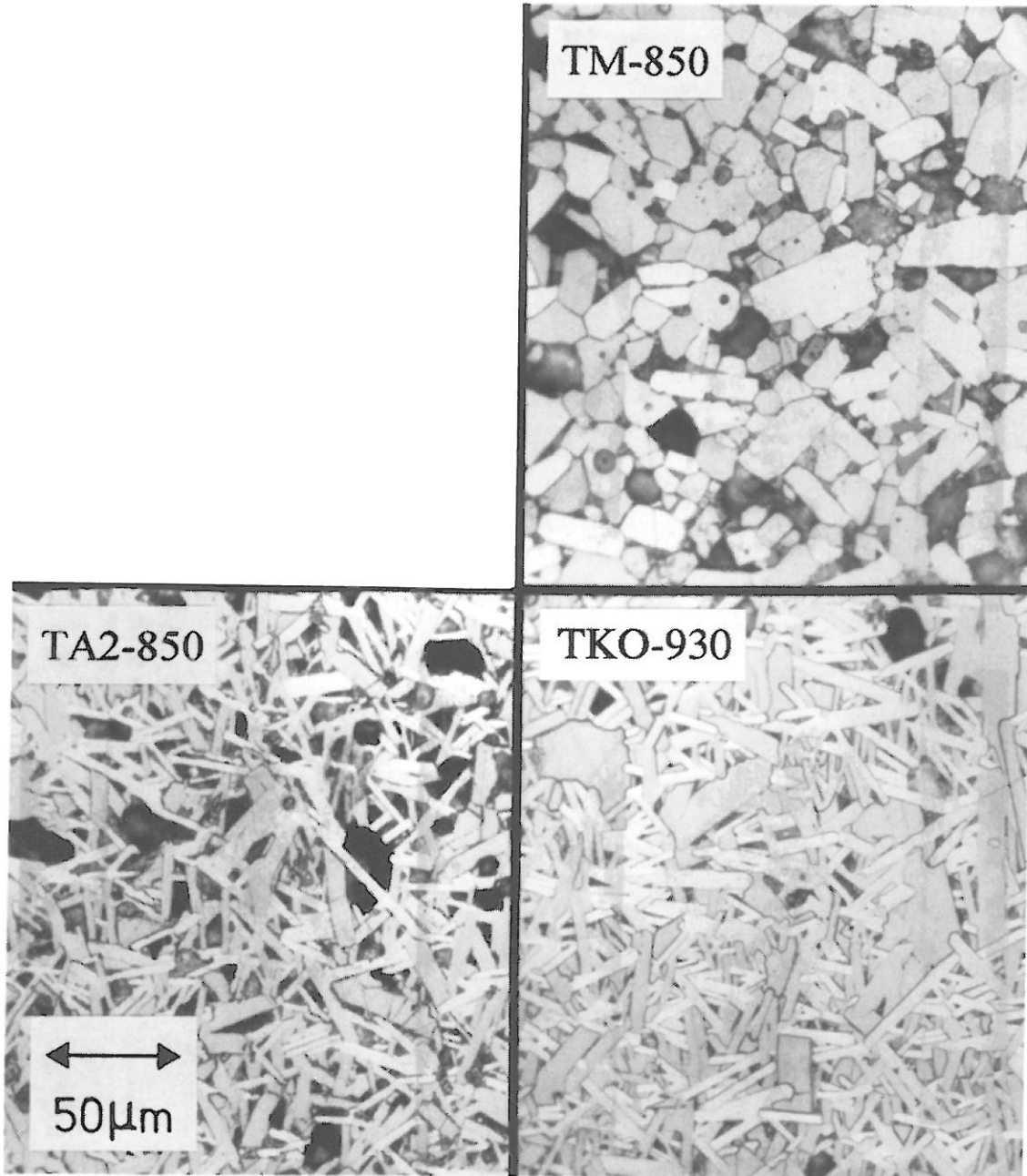


Figure 2: Optical micrographs of the orthorhombic TKO-930 and the tetragonal TM-850 and TA2-850 samples.

4. Superconducting single crystal X-ray diffraction results

Plate-like single crystals isolated from sample TLC1 were found to be superconducting. A.C. susceptibility measurements show a sharp transition at about 90 K. A triangular prismatic fragment was investigated by X-ray single-crystal diffraction (Mo K_{α} radiation, 2928 reflections measured, leading to 223 unique reflections with $I > 3\sigma(I)$ used for the structure refinement with 21 parameters in space-group $I4/mmm$). The lattice constants, from 34 centred reflections, showed a tetragonal metric within e.s.d.'s, $a=3.8714(5)$ Å, $c=23.269(7)$ Å. The thermal displacement parameters of both Tl and O(3), on site 4 e (0,0, z) were abnormally large and these sites were accordingly split, as previously suggested by Shimakawa et al. [1] and Liu et al. [4]. Better agreement indices ($R_w=1.95\%$, $S=1.405$) were obtained by delocalising the Tl on site 32 o (x,y,z), at 0.16 Å from the four-fold axis (the same distance is obtained with Tl on site 16 n (0, y,z) or 16 m (x,y,z)). The amount of Cu substituted on the Tl site was refined by constraining a full occupancy for this site and this leads to the refined stoichiometry $Tl_{1.94(2)}Ba_2Cu_{1.06(2)}O_6$. In an unconstrained refinement, viz. without considering copper substitution, the thallium occupancy refined to 0.1227(5), corresponding to $Tl_{1.96(1)}Ba_2Cu_1O_6$.

Table III: Atomic positional, thermal displacement and population parameters for $Tl_{1.94(2)}Ba_2Cu_{1.06(2)}O_6$.

Atom	Site	Occ.	x	y	z	U_{11}/U_{iso}	U_{22}	U_{33}
Tl	32 o	0.1213(8)	0.039(1)	0.017(3)	0.29735(2)	0.0089(2)	-	-
Cu(1)	32 o	0.0037(8)	0.039(1)	0.017(3)	0.29735(2)	0.0089(2)	-	-
Ba	4 e	1	0	0	0.08292(2)	0.0085(2)	U_{11}	0.0123(2)
Cu	2 b	1	0	0	1/2	0.0054(4)	U_{11}	0.0138(6)
O(1)	4 c	1	0	1/2	0	0.003(3)	0.010(3)	0.019(3)
O(2)	4 e	1	0	0	0.3832(2)	0.021(3)	U_{11}	0.007(3)
O(3)	16 n	0.25	0	0.085(4)	0.2110(3)	0.016(3)	-	-

5. Superconducting properties

The a.c. susceptibility was measured using a susceptometer previously described by Couach et al. [8] The excitation field working at a frequency of 35 Hz was set to 0.05 Oe_{rms} and 35 Oe. The earth field is compensated by a screen of μ -metal. The Meissner effect (field cooling) was measured with a r.f. SQUID magnetometer in an external field of 20 or 8.7 Oe. The Meissner flux expulsion ratio $f = -4\pi\chi_v$ ($B=H+4\pi M$, $\chi_v=M/H=\rho\chi_g$) was evaluated using an effective sample volume given by m/ρ , where m is the sample mass and ρ the X-ray density (≈ 8.0 g/cm³). For the data given in fig. 3, no geometric demagnetization factor D was taken into account. The corrected susceptibility should be $\chi_g = \chi_g^m / (1 - 4\pi D \rho \chi_g^m)$, where χ_g^m is the measured susceptibility. Fig. 3 also shows the Meissner field cooling (FC) and zero-field cooling (ZFC) measurements given without any correction.

The a.c. susceptibility of all 90 K superconductors exhibits a double transition at low excitation field as seen in fig. 3. The upper transition at 90 K does not give rise to any appreciable dissipation. The second step between 60 and 80 K is accompanied by a broad dissipation peak. Its shape and position depend strongly on the amplitude of the a.c. field [9]. This behaviour is characteristic of a granular superconductor with very weak inter-granular coupling [10]. The upper step gives the intra-grain transition temperature. Between this temperature and approximately 80 K, the magnetic field penetrates the sample because the surface cannot sustain the current required to completely expel the field. The lower transition is due to the weak inter-granular coupling (weak-link structure) [11, 12]. As expected, the second transition disappears in powder measurements [9] or using high excitation fields (see fig.3). For a granular sample, the analysis of the temperature behaviour of the FC measurement [13] predicts a ratio $R/\lambda(0)$ of about 30, where R is the radius of the superconducting grains and $\lambda(0)$ is the penetration depth at $T=0$ [13]. No significant difference was observed between FC measurements at 20 and 8.7 Oe. The value of the percentage of perfect screening at low temperature including the correction due to macroscopic demagnetization effects is given in table I.

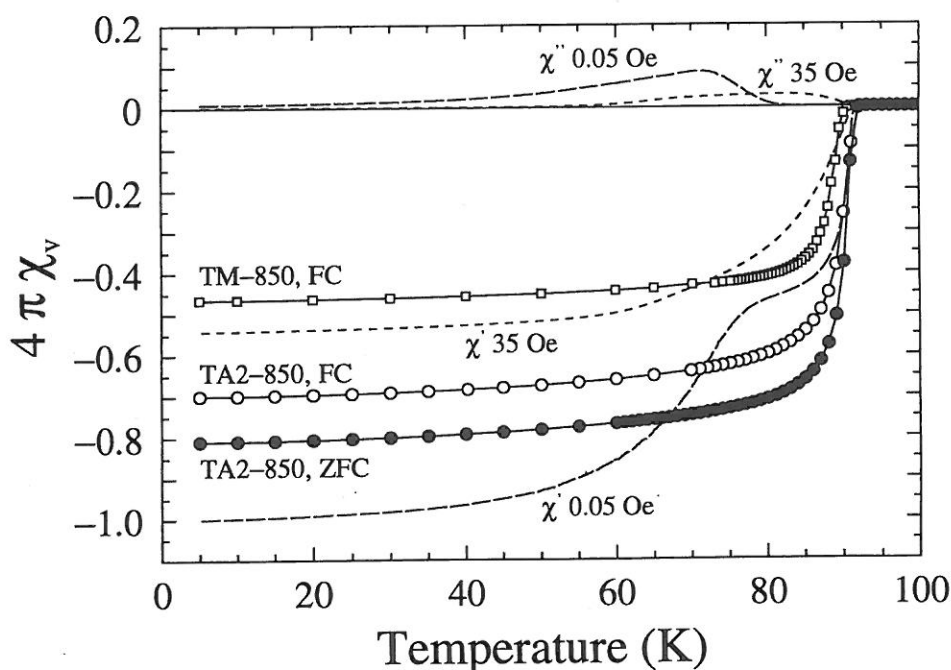


Figure 3: FC susceptibility at $H=20$ Oe for the sample TM-850 (open square). FC (open circle) and ZFC (black circle) at 8.7 Oe for the TA2-850 sample given without any correction. The a.c. susceptibility at 0.05 and 35 Oe is given for the sample TA2-850. Upper curves: imaginary part; lower curves: real part.

In view of the discussion following in the next section, it is interesting to mention some estimates on the superconducting volume fraction of tetragonal specimens. In the ZFC measurement (TA2-850, $H=8.7$ Oe), the sample effectively behaves as a superconducting powder. The expected diamagnetic signal at low temperature can then be evaluated using an averaged spherical demagnetization correction and a field penetration effect (here ≈ 0.1) resulting from the mean grain size. Comparison with the measured susceptibility yields a superconducting fraction f_s of about 60%.

At low temperature and in the limit of vanishing field amplitude in a.c. susceptibility measurements, the macroscopic demagnetization coefficient can be used (with some caution) and penetration effects should be negligible. The analysis yields in this case a porosity of 25%, in good agreement with the comparison of the macroscopic and X-ray densities (26%). At high field amplitudes, the behaviour should be again powder-like and the estimate based on the effective volume yields $f_s=67\%$. Finally, the Meissner flux expulsion, taking into account the macroscopic demagnetization correction, amounts to 63%. It is clear that the residual impurity phases cannot explain the reduced value of f_s and submicroscopic defects within the superconducting grains must be suspected.

6. Discussion

According to EDAX and plasma emission spectroscopy analysis, it is very unlikely that preferential thallium evaporation explains the mass losses during synthesis, i.e. 0.8% for orthorhombic and 1.5% for tetragonal samples. We conclude that, particularly in the latter case, oxygen losses are important. Tentatively, we may attribute the difference between 1.5 and 0.8% to oxygen losses alone. One then calculates a difference in oxygen content between high- T_c tetragonal and orthorhombic samples of 0.4 oxygen per formula unit. This estimate is in semi-quantitative agreement with measurements of Shimakawa et al. [1]. An extrapolation of their data to compositions showing $T_c=90$ K and $T_c=0$, respectively, indeed gives a difference of 0.3 oxygen per formula unit. It is interesting to note that high- T_c samples have an oxygen content O_x with x apparently lower than 6. This raises the important question of the nature of the hole doping [14]. Let us adopt the result of our single crystal X-ray refinement and write the composition for a $T_c=90$ K specimen $Tl_{1.94}Cu_{0.06}Ba_2Cu_1O_{5.93}$, where O_x with $x=5.93$ is suggested by extrapolation of Shimakawa's data. Assuming Tl^{3+} , this implies a formal valence on the copper site slightly below 2, which is somewhat disturbing. The possibility of a mixed oxidation state Tl^{3+} and Tl^{1+} has been discussed in the literature but NMR measurements by de Leeuw et al. [15] show that the predominant thallium oxidation state is +3.

Considering the rather severe constraints on the cation stoichiometry obtained in the present works, the actual oxygen distribution in superconducting 2201 crystals is likely to be the dominating factor governing the hole doping. A more or less pronounced inhomogeneity of the local oxygen concentration could be viewed as a tendency towards phase separation. A clear situation of this kind is well known in superconducting La_2CuO_4 . Given this hypothesis, the reduced superconducting volume fractions discussed in the preceding section would be explained in a natural way. Furthermore, the apparent absence of a measurable specific heat discontinuity at T_c [16] might be connected with the suggested inhomogeneous oxygen distribution.

7. Conclusions

We have found that the high temperature, high pressure route starting with $Tl_2Ba_2O_5$ and CuO produces large grained 2201 samples, the pressure effectively minimising thallium evaporation. Inert gas atmosphere is suitable for the synthesis of the tetragonal high- T_c phase. Various analyses show that cation vacancies have to be excluded but that a small copper substitution on the thallium site is possible. Therefore, some homogeneity domain $Tl_{2-x}Cu_x$ seems to exist. With respect to oxygen stoichiometry in the superconducting phase, we suggest that the concentration may be inhomogeneous on a sub-microscopic scale.

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