Superconductivity of Al/Al$_2$O$_3$ interface formed under shock-wave conditions

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Abstract. A mixture of powdered Al and Al$_2$O$_3$ has been subjected to a shock-wave pressure of $\approx$ 170 kbar, followed by vacuum-encapsulating and quenching of the product to liquid nitrogen. The ac magnetic susceptibility measurements of the samples have revealed metastable superconductivity with $T_c \approx 37$ K, characterized by glassy dynamics of the shielding currents below $T_c$. Comparison of the ac susceptibility and the dc magnetization measurements infers that the superconductivity arises within the interfacial granular layer formed between metallic Al and its oxide due to the shock-wave treatment.

1. Introduction

It is known that granular films of some superconductors exhibit enhancement of the superconducting transition temperature $T_c$, compared to that in the bulk, when the grain size is small enough. For example, in aluminum [1–3] this effect is about a double value of $T_c \approx 1.2$ K for the bulk. Moreover, it has been found that the films with comparable grain size evaporated at low temperatures in oxygen-free ambience [1] and at room temperature in oxygen atmosphere [3] demonstrate similar enhancement of the $T_c$ enhancement mechanism. The only role of oxygen has been considered to conserve small aluminium grains with aluminium oxide coating, thus stabilizing the fine-grain structure of the Al films, which results in stabilization of the enhanced $T_c$ [3].

A strong influence of structural disorder on the superconducting transition temperature was also emphasized by observation of highly enhanced superconductivity in Al films subjected to low-temperature ion (Si, Ge) implantation. The highest superconducting transition temperatures up to 8.35 K were observed in the films with high structural damage levels [4]. Metastable superconductivity with comparatively high superconducting transition temperature, $T_c \approx 45$ K, has been observed on bulk Al samples coated by aluminium oxide skin using the ac magnetic susceptibility measurements. These samples were prepared by surface oxidation of bulk aluminium under special conditions. The superconductivity of the samples was attributed to the interfacial layer Al/Al$_2$O$_3$ formed in between the metallic Al core and the oxidized sample surface. The superconducting samples turned out to be unstable at room temperature, as inferred from a decay of the superconducting transition after about 20-hours exposure of the vacuum-encapsulated samples to low temperature (77 K) provides their stabilization for infinitely
long time. A success in stabilization of the superconducting Al/Al₂O₃ interfaces by the low temperature quench has motivated our attempts to reproduce them by a method of shock-wave pressure load applied to the Al/Al₂O₃ mixture. This method has been recently approved for producing the metastable superconducting Mg/MgO and Cu/CuOₓ [5] interfaces. During the shock-wave impact, the stroke energy applied to the sample evokes relative displacements of local parts of the sample matter, resulting in a series of high-pressure shockwaves propagating throughout the sample within 10⁻⁶–10⁻⁹ s. The energy of the shock-waves leads to local, nonequilibrium overheat of the samples regions at the shockwave front, followed by their rapid cooling (quenching) as the shock-wave is passed, thus fixing the sample in the metastable state. Furthermore, highly non-equilibrium conditions caused by propagation of the high-pressure shock-waves in the sample can stimulate phase transitions or mechanochemical reactions inaccessible by any static high-pressure processes, resulting in new materials [6].

In this paper we report on metastable superconductivity at T_c ≈ 37 K of the mixture of Al and Al₂O₃ subjected to shockwave pressure of 170 kbar. Comparing the ac magnetic susceptibility and the dc magnetization measurement results, we conclude that the superconductivity arises within the interfacial layer formed between metallic Al and its oxide Al₂O₃. The superconducting Al/Al₂O₃ layer represents a structure of weakly linked superconducting grains.

2. Sample preparation and measurement techniques

The samples were prepared by means of flat-type shock-wave pressure setup described in detail earlier in [6]. The starting samples were tablets, 9.6 mm in diameter and 0.9 mm thick, of bulk 99.99%-pure aluminium disks covered by 0.2 mm layer of powdered 5–30 µm grain size, 99.99%-pure aluminium oxide—Al₂O₃. For preparing the superconducting Al/Al₂O₃ samples, the optimum value of the shock-wave pressure, within a 1 Mbar range, was found 170 kbar. After the shock-wave pressure treatment, the conservation cell was cut open on a lathe, the samples were extracted and vacuum-encapsulated at residual pressure 1–5 Pa into 5 cm-long quartz ampoules having 0.9 mm-thick walls and 6 mm outer diameter, and stored in liquid nitrogen to prevent their degradation. In total, the sample extraction and sealing procedure usually took less than 10 min. We need to emphasize here the importance of the samples to be vacuum-encapsulated after the shock-wave treatment: bare (unsealed) samples that were directly quenched into liquid nitrogen, did not demonstrate the desired effect (superconductivity). Apparently, this is due to destruction of the superconducting phase by adsorbed air on the sample surface during the sample cooling.

As a whole, twelve Al/Al₂O₃ samples, demonstrating qualitatively similar results of measurements, have been prepared under such conditions. For the reference, the samples consisting of bulk pure Al and of compacted Al₂O₃ powder were prepared separately under the same conditions. The dynamic magnetic susceptibility of the samples χ was measured using a mutual inductance ac susceptometer [7]. The amplitude H_ac of the driving field ranged from 0.22 to 10 Oe, the driving frequency ν from 300 Hz to 20 kHz, and the superimposed dc magnetic field H_dc up to 350 Oe. For the measurements, the vacuum-encapsulated sample was removed from liquid nitrogen and immediately placed in the pickup coil of the measurement insert, which was then dipped into a precooled cryostat. Any substantial warm-up of the sample that could lead to its degradation, has been carefully avoided during this minute-long procedure.

The static magnetic moment of the samples was studied by a Quantum Design SQUID magnetometer in the temperature range 5–70 K and static magnetic fields 30–300 Oe. Although the standard routine of loading the sample to the SQUID magnetometer is more lengthy (compared to that for the ac susceptometer) and can take up to 15 minutes until the sample is re-cooled, the subsequent ac susceptibility measurements have proved that the properties of the sample sealed in the evacuated ampoule survive such exposure to room temperature. Crystal structure of the samples was investigated at temperatures ≈ 80 and 300 K by x-ray diffraction.
measured using Oxford Diffraction Gemini R diffractometer equipped with a cooling system that enables the measurements in the flow of cold nitrogen gas. For the diffraction measurements, the sample was extracted from the quartz ampoule in the ambience of liquid nitrogen and immediately (within 5–10 s) mounted onto the precooled goniometer of the diffractometer.

3. Experimental results
The diffraction patterns of the shock-wave pressure treated Al/Al$_2$O$_3$ sample recorded at $T \approx 80$ K and at $T \approx 300$ K were found essentially the same, to within the thermal expansion factor. The diffraction pattern for $T \approx 300$ K is shown in figure 1. All the diffraction rings in the pattern are a superposition of the diffractions from polycrystalline Al/Al$_2$O$_3$ and Al crystal structures.

In contrast to the smooth diffraction rings from Al/Al$_2$O$_3$ structure, all the diffraction rings from Al in figure 1 include spots, apparently caused by larger crystallites of Al compared to those of Al/Al$_2$O$_3$. While the crystal unit cell parameters derived for the Al/Al$_2$O$_3$ crystal structure ($a = 4.76 \pm 0.01$ Å, $c = 12.99 \pm 0.01$ Å, space group R-3c) perfectly match the $\alpha$-alumina standard (reference: JCPDS no. 46-1212) [8], the crystal unit cell parameter for Al ($a = 4.08 \pm 0.01$ Å, space group Fm3m) was found to exceed the reported value 4.05 Å for the aluminium standard (reference: JCPDS no. 04-0787). The observed discrepancy is a consequence of the shock-wave pressure effect on the Al crystal structure.

4. Dynamic magnetic susceptibility
The dynamic magnetic susceptibility measurements of all the twelve Al/Al$_2$O$_3$ samples prepared by $\approx 170$ kbar shockwave pressure loading have revealed qualitatively similar results. Each cycle of T measurements has started from a cool-down of the Al/Al$_2$O$_3$ sample to 5.5 K at zero magnetic fields $H_{ac}$ and $H_{dc}$. Quite remarkably, as $H_{ac}$ is applied at constant temperature after the cool-down, develops to the equilibrium value monotonously in time, $t$, towards the enlargement of diamagnetism. The time evolution of $\chi$ measured at frequency = 316 Hz, $H_{ac}$ = 0.22 Oe and $H_{dc}$ = 0 is illustrated in figure 2. $\chi$ was found to relax exponentially to ground.
Figure 2. Time evolution of $4\pi \chi'$ at $T = 5.5$ K for the vacuum-encapsulated shock-wave pressure treated Al/Al$_2$O$_3$ sample. Inset—temperature dependencies of $4\pi \chi'(T)$ measured before (curve 1) and after (curve 2) the sample exposure for $\approx 25$ hours to room temperature.

diamagnetic state as $a + b \exp(t/\tau)$, shown in figure by a solid line, where $a$, $b$ and $\tau$ are fit parameters. The extracted time constant, $\tau = 30 \pm 2$ min, is practically independent on frequency for the range 0.3–20 kHz.

We need to emphasize that the observed $\chi(t)$ dependence is not related to possible relaxation of the sample temperature towards equilibrium (5.5 K), because the $\chi(t)$ relaxation curves are reproducible regardless of how long the sample is kept at 5.5 K before $H_{ac}$ is switched on and the measurements are started.

After the $\chi(t)$ measurements performed over $\approx 3\tau$ period at $T = 5.5$ K, the $\chi(T)$ dependence was measured upon heating at the rate of 1–1.5 K/min (slower heating rate made no visible change to the measurement result). The measured $\chi(T)$ dependence is shown by curve 1 in the Inset of figure 2. In this plot, the drop in $\chi(T)$ curve at 5.5 K corresponds to the $\chi(t)$ relaxation process, shown in figure 2. A step-like anomaly in $\chi(T)$ is observed at $T_c \approx 37$ K ($H_{ac} = 0.22$ Oe, $H_{dc} = 0$ Oe), signifying a phase transition in the sample at this temperature. In order to exclude the influence of the $\chi(t)$ relaxation process on the $\chi(T)$ result, all subsequent $\chi(T)$ measurements were performed according to the measurement cycle described above (cool-down to 5 K—turn on $H_{ac}$—1.5 hour delay—measure $\chi'(T)$ upon heating).

The $\chi(T)$ dependencies measured in a static magnetic field, $H_{dc}$, are shown in figure 3. According to curves 1–3, an increase in $H_{dc}$ suppresses the anomaly in $\chi(T)$. Increasing the driving ac magnetic field amplitude, $H_{ac}$, gives a similar effect, as shown in figure 4. Figure 5 shows the temperature dependencies of $\chi'$ and $\chi''$ measured at frequencies from 0.3 to 20 kHz. One can see in figure 5 that $T_c$ is essentially frequency independent, while the shapes of the $\chi'(T)$ and $\chi''(T)$ curves at the phase transition change dramatically with the frequency.

After completion of the measurements described above, the insert with the Al/Al$_2$O$_3$ sample was finally kept for $\approx 25$ hours at room temperature. The following measurements have shown, first of all, no time dependence of $\chi'(t)$ at 5.5 K. Furthermore, the $\chi(T)$ dependence of the room-temperature-annealed Al/Al$_2$O$_3$ sample does not exhibit a step-like anomaly and is independent on $H_{ac}$ and $H_{dc}$, within the ranges used previously (curve 2 in the inset of figure 2, curves 4 in
Figure 3. Temperature dependencies of the real (a) and the imaginary (b) parts of $4\pi \chi$ for the Al/Al$_2$O$_3$ sample measured under the dc magnetic field $H_{dc} = 0.134$ Oe and 350 Oe (curves 1 to 3, respectively). Curves 4 correspond to the same sample exposed for $\approx 25$ hours to room temperature. In addition, now $\chi'(T)$ and $\chi''(T)$ dependencies are practically identical to those of the pure aluminium sample, subjected to the shock-wave pressure treatment under the same conditions. Moreover, a temperature independent $\chi'(T)$ without any anomaly in the experimental temperature range was found for the shock-wave pressure treated aluminium oxide (Al/Al$_2$O$_3$) sample. Therefore, all the results suggest that the phase responsible for the observed anomaly in $\chi'(T)$ of the Al/Al$_2$O$_3$ sample is related to the interfacial area formed between the Al and Al/Al$_2$O$_3$ phases, and that this phase is unstable at room temperature. In contrast to the ac magnetic susceptibility, the dc magnetic moment of the shock-wave pressure treated Al/Al$_2$O$_3$ samples measured using a SQUID magnetometer in a standard zero-field-cooled and field-cooling regimes, revealed no sign of the magnetic anomaly. At temperatures from 5 to 70 K, the Al/Al$_2$O$_3$ samples demonstrated a nearly temperature-independent dc magnetic susceptibility ($\approx 10^{-6}$ cm$^3$/g) in static magnetic fields $H_{dc} = 30$–300 Oe.
Figure 4. Temperature dependencies of the real (a) and the imaginary (b) parts of $4\pi \chi$ for the Al/Al$_2$O$_3$ sample measured with the amplitude of the ac driving field $H_{ac} = 0.22, 2.33, 4.67$ and 9.36 Oe (curves 1 to 4, respectively). Curves 5 correspond to the same sample exposed for $\approx 25$ hours to room temperature.

5. Discussion
In the ac magnetic susceptibility measurements, the $\chi'$ response to the ac magnetic field is a function of the skin depth,

$$\sigma = \frac{c}{2\pi \sqrt{\sigma \mu \nu}}$$

where $\sigma$ and $\mu$ are, respectively, the electric conductivity and magnetic permeability of the material, $\nu$ is the ac magnetic field frequency and $c$ is velocity of light in vacuum. As mentioned above, no anomalies in the dc magnetization of the Al/Al$_2$O$_3$ samples have been found in the temperature range 5–70 K. Since the Al/Al$_2$O$_3$ samples were found to be nonmagnetic ($\mu \approx 1$) at these temperatures, the only reason for the observed step-like anomaly in $\chi'(T)$, shown by curve 1 in the Inset of figure 2, is a sudden change of the electric conductivity $\sigma$ of the samples, which we attribute to a superconducting transition.

This assumption is justified by the effect of suppression of the anomaly by magnetic field (figures 3 and 4). The anomaly in $\chi(T)$ observed at $T_c \approx 37$ K for $H_{ac} = 0.22$ Oe and $H_{dc} = 0$, reduces in size and shifts to lower temperature with increasing either $H_{dc}$ (curves 1–3 in figure 3) or $H_{ac}$ (curves 1–4 in figure 4). The $\chi'(T)$ and $\chi''(T)$ dependencies presented in figures 3 and
Figure 5. Temperature dependencies of the real (a) and imaginary (b) parts of $4\pi \chi$ for the Al/Al$_2$O$_3$ sample measured at frequencies 0.316, 1.58, 2.24, 16.7 and 20.2 kHz (curves 1 to 5, respectively).

4 are typical for superconducting materials which implies a superconducting transition in the Al/Al$_2$O$_3$ sample. We note that none of the constituents of the sample, neither metallic Al nor $\alpha$-Al$_2$O$_3$ are superconductors in the bulk in the experimental temperature range. Moreover, none of them, taken separately and subjected to the shock-wave pressure treatment, demonstrate any anomaly in $\chi(T)$. We conclude therefore that the superconductivity in the shock-wave pressure treated Al/Al$_2$O$_3$ sample is related to the interfacial layer formed between aluminium oxide and metallic aluminium phases.

One can see in figures 3 and 4 that at temperatures well below $T_c$, $4\pi \chi'(T) \sim -1$ and $\chi''(T) \sim 0$. We conclude therefore that the superconducting interface formed within the interfacial Al/Al$_2$O$_3$ layer is not a closed surface enveloping the sample, which would trap the magnetic flux and keep it constant ($4\pi \chi'(T) = -1$, $\chi''(T) = 0$), but rather consists of superconducting grains embedded into a non-superconducting host matrix and weakly linked by narrow, non-superconducting bridges. Besides, the zero-field-cooled regime of the dc magnetic moment measurement has shown no sign of the superconducting transition at all. Therefore, the superconducting grains are apparently small, less than the London penetration depth, $\lambda$. In this assumption, in the dc magnetic moment measurements, the weak links result in a rapid decay of the intergrain shielding current after applying the dc magnetic field, while the intragrain superconducting
currents give a negligible contribution to the shielding of magnetic field due to small (sub-λ) size of the grains, thus resulting in nonmagnetic (ν ≈ 1) superconducting state of the sample.

On the contrary to the dc magnetization measurements, the alternating magnetic field used in the ac magnetic susceptibility measurements maintains the intergrain shielding current. This enables the superconductivity to be detected even in discontinuous, energy dissipative loops, consisting of weakly linked superconducting sub-λ-grains. Of course, the diamagnetic state of such structures is quite obviously far from ideal (4πχ′(T) = −1 and χ″(T) = 0), as observed for the Al/Al2O3 sample. The evolution of χ′(T) with frequency, shown in figure 5, is qualitatively similar to that one for Mg/MgO and Cu/CuOx [5] shock pressure treated samples. As one can see in figure 5a, the step in χ′(T) at Tc ≈ 37 K becomes bigger as the driving frequency increases from 0.316 to 1.58 kHz (curves 1–2) and diminishes with further frequency increase (curves 3–5). This can be explained by a superposition of normal and superconducting shielding currents, contributing to χ′(T) in the Al/Al2O3 sample.

Consider first the χ′(T) response at T ≈ 37 K, diminishing with the frequency increase (ν ≲ 1.58 kHz, curves 3–5 in figure 5a). This effect is well known for bulk metallic superconductors: in the normal state, increasing the ac magnetic field frequency leads to diminishing skin depth δ, hence a bigger diamagnetic signal. As a result, in the high frequency limit, the normal metal just above Tc is nearly as diamagnetic as the superconductor just below Tc which makes the superconducting transition indistinguishable in χ(T).

On the other hand, intergranular weak links in the superconducting Al/Al2O3 interfaces can be considered as electric capacitors connected in series into the shielding intergrain supercurrent loops. Obviously, the higher is frequency, the better the superconducting grains are linked, hence the stronger is the superconducting shielding. Apparently, this explains the growth of the χ′(T) response at Tc ≈ 37 K at frequencies up to 1.58 kHz (curves 12 in figure 5a). The two competing contributions superimpose in the studied Al/Al2O3 sample to give a maximum of the χ′(T) response to the superconducting transition at ν ≈ 1.58 kHz.

The evolution of χ″(T) with frequency is shown in figure 5b. At low frequencies (curves 1–2), χ″(T) exhibits a step-like rise at cooling below Tc ≈ 37 K, while at high frequencies (curves 4–5) a step-like drop is observed instead. At the crossover frequency ν = 2.24 kHz (curve 3 in figure 5b, curve 1 in figures 3b and 4b) a cusp-like anomaly in χ″(T) is observed at Tc. We explain the observed frequency behavior of χ″(T) by the vortex dynamics influenced by the ac drive field. At low frequencies the ac magnetic field oscillations are slow enough to enable the vortex motion in response to the variation of the ac magnetic field. This vortex motion contributes additionally to the energy dissipation caused by the normal currents, giving rise to a step-like increase of χ″(T) upon cooling the sample through Tc ≈ 37 K (curves 1–2 in figure 5b). At higher frequencies the drive field oscillations are too fast to disturb the vortex system, which enables the energy dissipation through the vortex motion.

In this case a step-like decrease of χ″(T) is observed at Tc ≈ 37 K upon cooling (curves 4–5 in figure 5b), which reflects the shielding of the energy-dissipative interior of the sample by the supercurrents. As it was mentioned above, the superconducting interfaces in the Al/Al2O3 sample are unstable at room temperature (figures 2, 3 and 4). The reason for such instability is apparently the aluminium/oxygen ionic diffusion processes activated at room temperature in the Al/Al2O3 interfaces, which destroy the superconductivity in the sample. The T-dependencies of χ′(T) and χ″(T) measured on the degraded Al/Al2O3 samples (curves 4 in figure 3, curves 5 in figure 4) are typical for normal nonmagnetic metals. Namely, as the temperature decreases, the conductivity of the sample increases monotonically that leads to a decrease in the skin depth, thus to a monotonic decrease in χ′. At low temperatures, the electric conductivity becomes more flat in temperature, and χ′(T) sets constant. In turn, χ″ is also a function of δ, χ″ is small when σ ≫ r (insulator) and σ ≪ r (ideal metal), and is maximum when the conductivity matches the condition σ = r, where r is the sample depth. This broad maximum can be observed on curve 4.
in figure 3b and curve 5 in figure 4b at $T_{\text{max}} \approx 29$ K. Following the $\sigma = r$ condition, in a sample with negative $d\sigma = dT$ (i.e. a metal) the maximum in $\chi''(T)$ shifts to higher temperature with increasing frequency, according to equation above. This explains the change of the $\chi''(T)$ slope with frequency at $T < T_c$ observed in figure 5b: obviously, $T_{\text{max}} > T_c$ for curves 1–3, while for curves 4, 5 $T_{\text{max}} < 40$ K.

6. Nature of the observed superconductivity

Although the room-temperature exposure of the Al/Al$_2$O$_3$ samples leads to a dramatic decay of the superconducting fraction, no corresponding change has been detected in the x-ray diffraction patterns. The fraction of the superconducting phase is therefore too small to be detected by the x-ray diffraction technique. In addition, none of the constituents of the sample, neither metallic Al nor $\alpha$-Al/Al$_2$O$_3$, taken separately and subjected to the shock-wave pressure treatment, demonstrate any anomaly in $\chi(T)$. We believe therefore that the superconductivity in the shock-wave pressure treated Al/Al$_2$O$_3$ samples is related to the interfacial layer formed between the aluminium oxide and metallic aluminium phases. Comparison of the results of the ac susceptibility and the dc magnetization measurements suggests that the superconducting Al/Al$_2$O$_3$ interface is not a continuous layer but consists of weakly linked small superconducting grains embedded into a non-superconducting ambience.

Among various models of enhanced superconductivity in granular films, dealing with quantization of electron levels in small grains or extra electron-electron attractive interaction via the polarization wave [9], numerous studies have inclined to explain the phenomenon by the effects of softening of the phonon spectra at the surface of small aluminium grains separated by tunnel barriers of aluminium oxide. However, the observed value of $T_c \approx 37$ K for the shock-wave pressure treated Al/Al$_2$O$_3$ samples is apparently too high to be explained by the surface phonon softening effect.

Furthermore, the multiformity of aluminium oxides could give reasonable grounds to attribute the superconductivity in the Al/Al$_2$O$_3$ samples to some unknown superconducting aluminium oxide structure, unstable under the normal conditions and located at the interfacial areas in the Al/Al$_2$O$_3$ sample. However, the interfacial superconductivity has been discovered for other similar objects based on metals of various groups and their oxides (Cu/CuO [5]). From the generality of the phenomenon, we suppose that the observed superconductivity is directly related to specific oxygen states located at the superconducting metal-metal oxide interface, rather than some unique properties of chosen metals.

This assumption is consistent with the statements of [10] where oxygen interfacial anions of a metal oxide have been emphasized to play a dominant role in the formation of the metal/metal oxide interfacial superconductivity. More specifically, the local electron pairs (LEPs) are suggested to appear in the oxygen anion subsystem of the metal oxide at the metal/metal oxide interface. The LEPs penetrate into the adjacent metal environment which allows them to move along the interface, thus forming a superconducting condensate. For example, under certain conditions the onset temperature of Bose-Einstein condensation in Cu/CuO interface was estimated to reach $T_c \approx 1000$ K [10].

The observed room temperature instability of the superconducting metal-metal oxide interfaces is apparently caused by temperature activated diffusion of the oxygen and metal ions in the metal-metal oxide interfacial layer. According to [10], we suppose that the diffusion process implies a tendency of the O$^{1-}$ interfacial state responsible for the metal/metal oxide interfacial superconductivity to approach the equilibrium O$^{2-}$ state typical for non-superconducting metal oxides.

Alternatively, consider isolated nanometer-sized metallic clusters which may spontaneously arise in the metal-oxide interfacial layer formed during either the shock-wave pressure treatment of a metal-oxide mixture or the surface oxidation of a bulk metallic sample. Delocalized electrons
of such clusters are expected to form a narrow, partially filled energy band at the Fermi level, resulting in a new hypothetical family of high-$T_c$ superconductors [11]. Besides, two-dimensional metal/oxide interfacial areas may play a role of asymmetric confining potentials in the system of free electrons, resulting in the lack of spatial inversion symmetry at the interfaces. This may stimulate a topological change of the Fermi surface due to the spin-orbit splitting and lead to the enhanced superconductivity [11].

Acknowledgments
The work has been supported by RFBR grant No. 13-02-01217.

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