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Thermal conductivity of mica at low temperatures

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The thermal conductivity of muscovite and phlogopite has been measured over a temperature range of 3 to 320 K, in directions parallel and perpendicular to the cleavage planes. Both materials showed anisotropic behaviour. The room temperature values for muscovite and phlogopite, respectively, were 4.05 and 3.7 W m^{-1} K^{-1} for conductivity parallel to the planes, and 0.46 and 0.44 W m^{-1} K^{-1} perpendicular to the planes. Plots of the variation of thermal conductivity with temperature for both directions in the two materials show a gradual rise in conductivity as the temperature is lowered below room temperature. All four curves reach a peak at about the same temperature of 15 K. The peak values obtained were 12.4 and 7.25 W m^{-1} K^{-1} parallel to the planes, and 4.7 and 2.05 W m^{-1} K^{-1} perpendicular to the planes.

1. Introduction

Mica is an important technological material because of its properties of easy cleavage combined with sheet strength. It is a good electrical insulator and is almost transparent (energy gap 3.5 to 4 eV). Mica finds use in electrical components as an insulator and as a dielectric, and as a window in r.f. and infra-red radiation applications. It is also used as a substrate for evaporated thin films.

In addition to the anisotropy in structure, mica also shows anisotropic behaviour in electrical and thermal conductivities and thermal expansion. This paper reports on measurements of the thermal conductivity of two varieties of mica, within the temperature range 3 to 320 K. The thermal conductivity in any direction parallel to the cleavage plane will be denoted $\kappa_{\parallel}$ and that perpendicular to the plane as $\kappa_{\perp}$.

1.1. Structure

The term mica refers to a group of monoclinic silicate minerals having the general formula:

$$(K, Na, Ca)X_n AlSi_3 O_{10}(OH, F)_2$$

where the items in brackets are alternative selections. The two varieties used in these experiments were muscovite which has $X_n = Al_2$, and phlogopite with $X_n = Mg_3$.

Mica crystallizes in the form of sheets composed of two layers of (Si, Al)O_4 tetrahedra which sandwich octohedrally co-ordinated Mg, or Al cations. The tetrahedra link together to form a hexagonal arrangement within the plane of the layers. The sheets thus obtained are negatively charged, the complex ion having the form $[X_n Al\, Si_3 O_{10} (OH)_2]^-$, and in mica the sheets alternate with planes of cations such as K^+, Na^+ or Ca^{2+} to give an electrically neutral material. The sheet thickness is about 0.66 nm and the repeat distance is about 1 nm or a multiple of 1 nm, depending on the stacking sequence of successive sheets. Mica cleaves along the planes of the sheets, relatively easily in air and more so under water [1]. More complete descriptions and illustrations of the structure of mica will be found in [2] and [3].

1.2. Previous work

Whilst no results of thermal conductivity measure-

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ments on mica below a temperature of 188 K have been published, several measurements have been done at higher temperatures.*

Jannettaz [4] measured the anisotropy ratio $\kappa_{\|}/\kappa_{\perp}$ on several mica samples at room temperature by plotting isothermal contours on a heated sample in which steady state conditions had been reached. Metsik [5] also determined the ratio $\kappa_{\|}/\kappa_{\perp}$ at room temperature, but by measuring the cooling rate of samples of different dimensions. He also calculated the conductivity maximum ($\kappa_{\|}$) using the heat capacity and density, and so also derived $\kappa_{\perp}$.

The steady state heat flow method was used by Powell and Griffiths [6] who made transverse ($\kappa_{\perp}$) measurements on phlogopite and muscovite from 323 to 873 K. Goldsmid and Bowley [7] used the same method to measure $\kappa_{\|}$ in phlogopite between 188 and 320 K and also confirmed their results using a thermal diffusivity technique. Most recently, Egorov *et al.* [8] measured $\kappa_{\|}$ in muscovite and phlogopite from 300 to 600 K as well as measurements on synthetic micas.

For the related parameter of thermal expansion, several measurements at low temperatures have been made. Early measurements down to a temperature of 20 K are summarized in [9]. Goldstein and Post [10] have measured thermal expansion of muscovite between 83 and 423 K and Kitajima and Daimon [11] measured in synthetic phlogopite from 273 to 1200 K.

2. Experimental details

2.1. Sample preparation and mounting

For measurements of $\kappa_{\|}$, four samples were prepared. These consisted of a sample of Madagascan phlogopite, one of Australian muscovite mined at Broken Hill, N.S.W., and two samples of Indian muscovite cut from the same piece. Each sample was made up as a book of sheets glued together with a thin layer of GE 7031 varnish between each sheet. Each sample was 14 mm long, about 4 mm wide and 3 to 4 mm thick. Each piece was cut using a dental cutting machine (which blows a jet of aluminium oxide powder abrasive) with the longest dimension directed along an axis of crystal symmetry within the plane, the crystal being oriented by the Laue X-ray method. The second Indian muscovite sample was oriented at 30° to the first in order to test for anisotropy of κ in directions along the cleavage plane. The above powder blasting method was chosen since it did not seem as susceptible to causing separation of layers as other methods did.

The samples had small copper blocks torr-seal glued to each end, one to house a 47 Ω $\frac{1}{8}$ W heater resistor and the other to be soldered to the heat sink. The resistor was embedded with torr-seal in a small hole drilled in the heater block.

For $\kappa_{\perp}$ measurements, two discs of a mica sample were clamped together with a copper disc as heater sandwiched between them. Clamping was necessary because initial readings showed that reproducible results could not be obtained for $\kappa_{\perp}$ with free standing samples when the temperature was cycled between 77 and 300 K. The clamping device was made from OFHC copper and acted as the heat sink for each disc of mica.

Two sets of discs were cut using the powder abrasive cutter and a slowly rotating turntable. One set was cut from Australian muscovite and the other from phlogopite, each disc being about 9 mm diameter and 0.7 mm thick. The thermal resistance between each mica surface and the copper was reduced by inserting a thin sheet of indium about 0.1 mm thick between each interface.

The density of the phlogopite and the two varieties of muscovite material were measured using the hydrostatic method of weighing in air and in distilled water.

2.2. Method

A cryostat consisting of an outer can and inner pot (see White [12]) was used for the measurements at low temperatures. Measurements were performed under adiabatic conditions with the pressure of the region between the pot and can reduced to about 2 mPa (10^{-5} Torr) by an oil diffusion pump. The sample heat-sinks were soldered with Wood's metal to the bottom surface of the pot and enshrouded by a radiation shield which screwed onto the pot.

The temperature of the pot relative to the outer can and refrigerant liquid bath could be varied by two means. To obtain temperatures

*Since submission of this paper, Falco [20] has reported measurements of $\kappa_{\|}$ on two samples of muscovite for the temperature range 1.5 to 4.2 K. There appears to be good agreement between his results and ours for the temperature region where results overlap.

below the bath temperature, refrigerant liquid was introduced into the pot via a needle valve, and the vapour pressure within the pot controlled using a rotary pump and Cartesian manostat system. For temperatures above the bath temperature a constantan heater wound around the pot was energized, the supply of power being regulated by a Harwell Temperature Controller. For the temperature range 3 to 60 K liquid helium was used as refrigerant and for 60 to 100 K liquid nitrogen. For temperatures above 100 K a series of solid/liquid isothermal baths were used, to reduce radiation loss effects.

The heat sink temperature was monitored using a germanium thermometer for the region below 30 K and a platinum thermometer above 30 K. During the first liquid helium run, when measuring the four $\kappa_{\parallel}$ samples, discrepancies arose between temperature readings of the germanium thermometer, platinum thermometer and the Temperature Controller's gold–iron/chromel thermocouple sensor. So for the later runs, measuring $\kappa_{\perp}$, two germanium and two platinum thermometers were mounted on the pot as a calibration check.

Temperature gradients developed across samples were measured using Au–0.07 at.% Fe versus chromel-p differential thermocouples. For $\kappa_{\parallel}$ measurements the thermocouple junctions were torr-seal glued into grooves cut across the sample. In addition, the temperature of the colder junction of the Australian muscovite sample was measured relative to the heat sink with a gold–iron/chromel thermocouple. For $\kappa_{\perp}$ two thermocouples were used to indicate heater and clamp temperature differences, but were sited differently for the muscovite and phlogopite readings. For muscovite, one thermocouple was connected between the heater and the base of the pot and the other from the clamping cross-bar to the pot base.

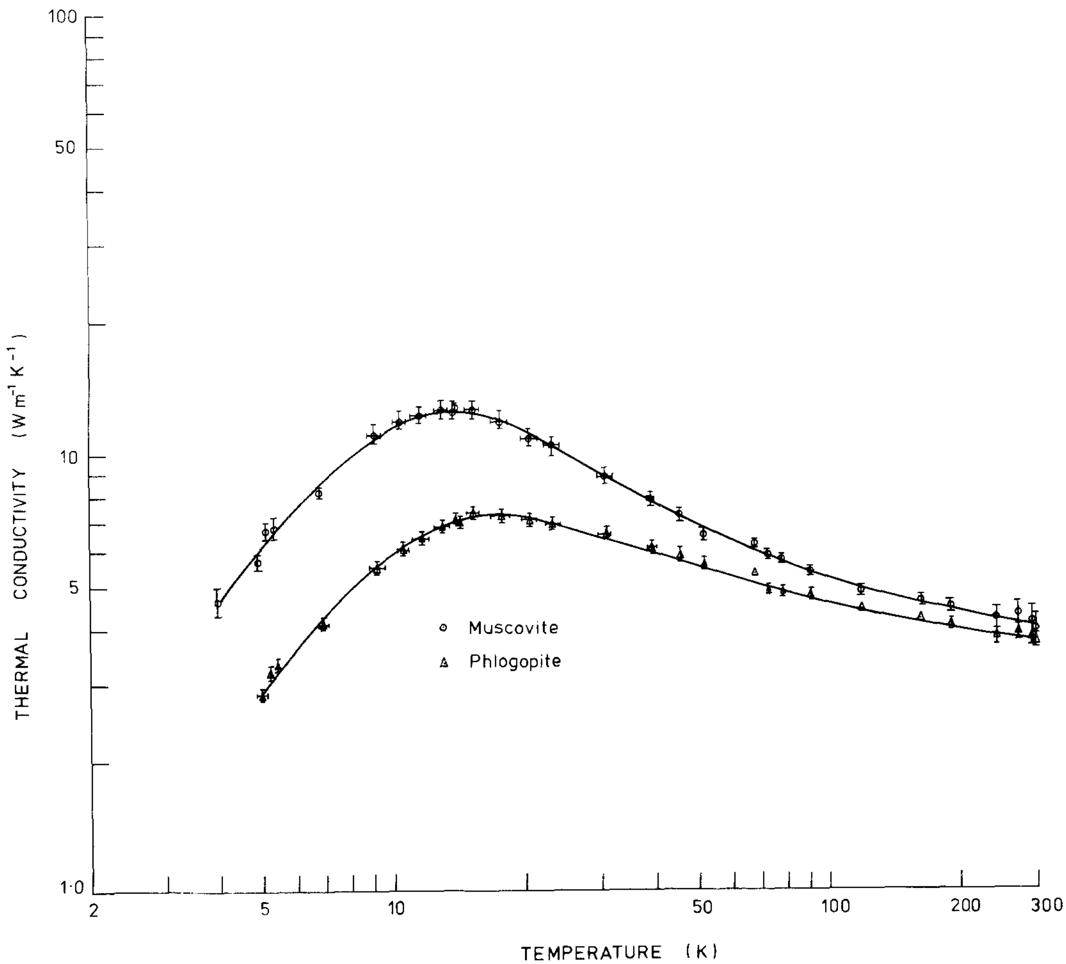

Figure 1 Thermal conductivity along planes.

For phlogopite, the thermocouples were connected between the heater and the section of clamp immediately adjacent to each disc of the sample.

Thermocouple voltages were measured using a Leeds and Northrop K-5 potentiometer. Voltages developed across thermometers, current monitoring standard resistors and sample heater resistors were measured with a Fluke DVM. For the $\kappa_{\parallel}$ measurements an effort was made to reduce heat losses caused by conduction along the heater current and voltage wires. This was done by including a fifth sample with a thin copper rod as a heater block around which were wrapped the heater wires from the four samples. The heater wiring was arranged so that the heater of this dummy sample was in series with the energized sample heater, so that the rod temperature would approximately match the sample heater temperature.

The effect of finite thermal resistance of the copper clamp used in $\kappa_{\perp}$ measurements was accounted for by analysing the thermal circuit for both configurations of thermocouple attachment and calculating $\kappa_{\perp}$ using published values of κ for OFHC copper [13].

At temperatures above 100 K, radiation loss can become an appreciable factor. It was neglected for the $\kappa_{\perp}$ measurements because the exposed surface area of the mica and heater discs was small. The radiative component from the heater faces to the heat sinks through the mica was also calculated and found to be negligible for the temperature range of interest. The radiation loss from the longer samples used in the $\kappa_{\parallel}$ experiment was estimated by measuring the heat flow from a heater plus sample suspended free, and from the heater block alone, using the same heater to base temperature difference. This was

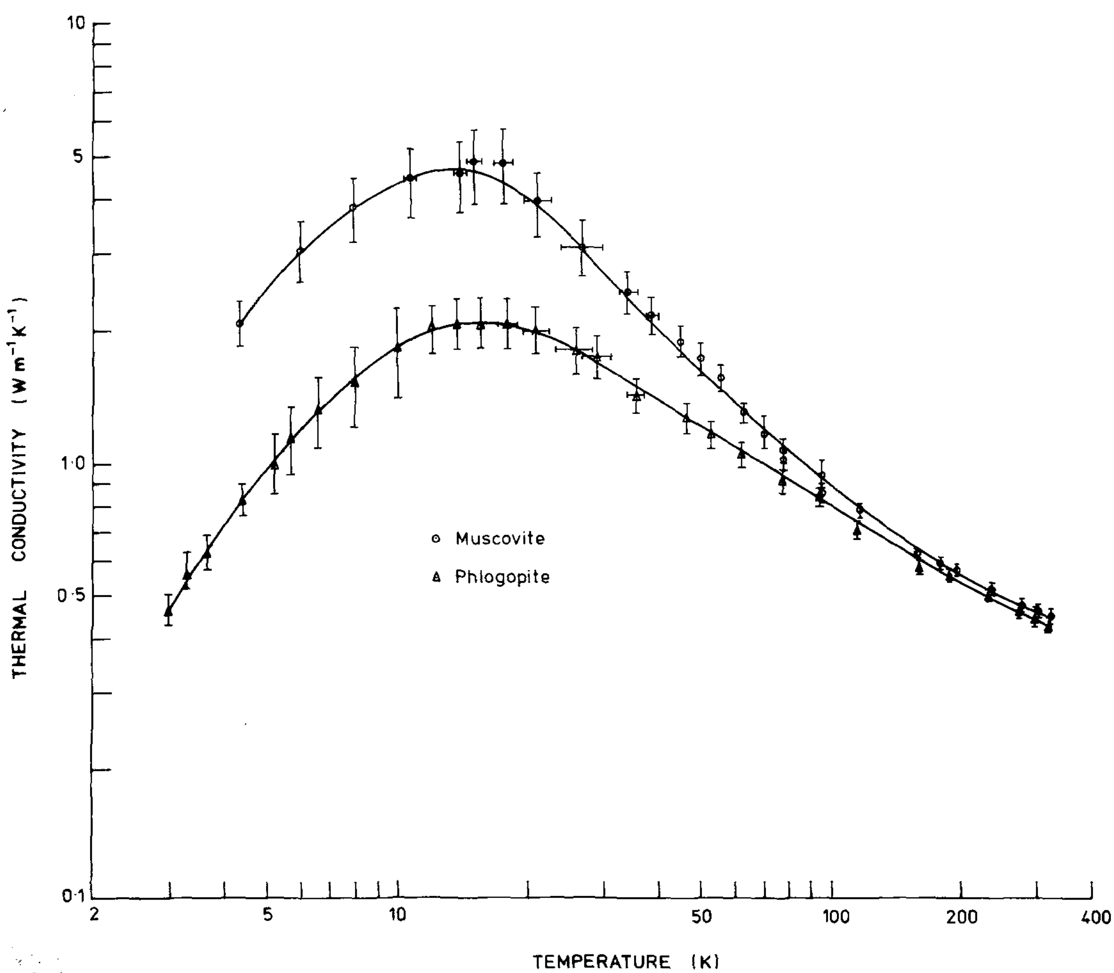

Figure 2 Thermal conductivity perpendicular to planes.

carried out on the Australian muscovite and the phlogopite samples and was repeated for several base temperatures between 77 and 320 K.

3. Results

Figs. 1 and 2 show the temperature variation of $\kappa_{\parallel}$ and $\kappa_{\perp}$, respectively, for the phlogopite and Australian muscovite samples. The temperature variation of the anisotropy ratio $\kappa_{\parallel}/\kappa_{\perp}$ is shown in Fig. 3. Table I lists some of the noteworthy results indicated by the graphs, and also the density values.

Error bars have been drawn on the experimental points of Figs. 1 and 2 where errors are estimated to be significant. Only those errors which vary with temperature have been included; static errors such as those due to dimension measurements amount to about 5%.

The main sources of error were: (1) small temperature gradients at low temperatures, especially for the transverse measurements; (2) calibration difficulties with the germanium and platinum thermometers over the range 20 to 40 K. Significant errors occur in $\kappa_{\parallel}$ at higher temperatures due to uncertainties in the radiation loss calculations.

Figs. 1 and 2 indicate that smooth curves can be fitted quite easily to the experimental points, so the error limits have probably been overestimated.

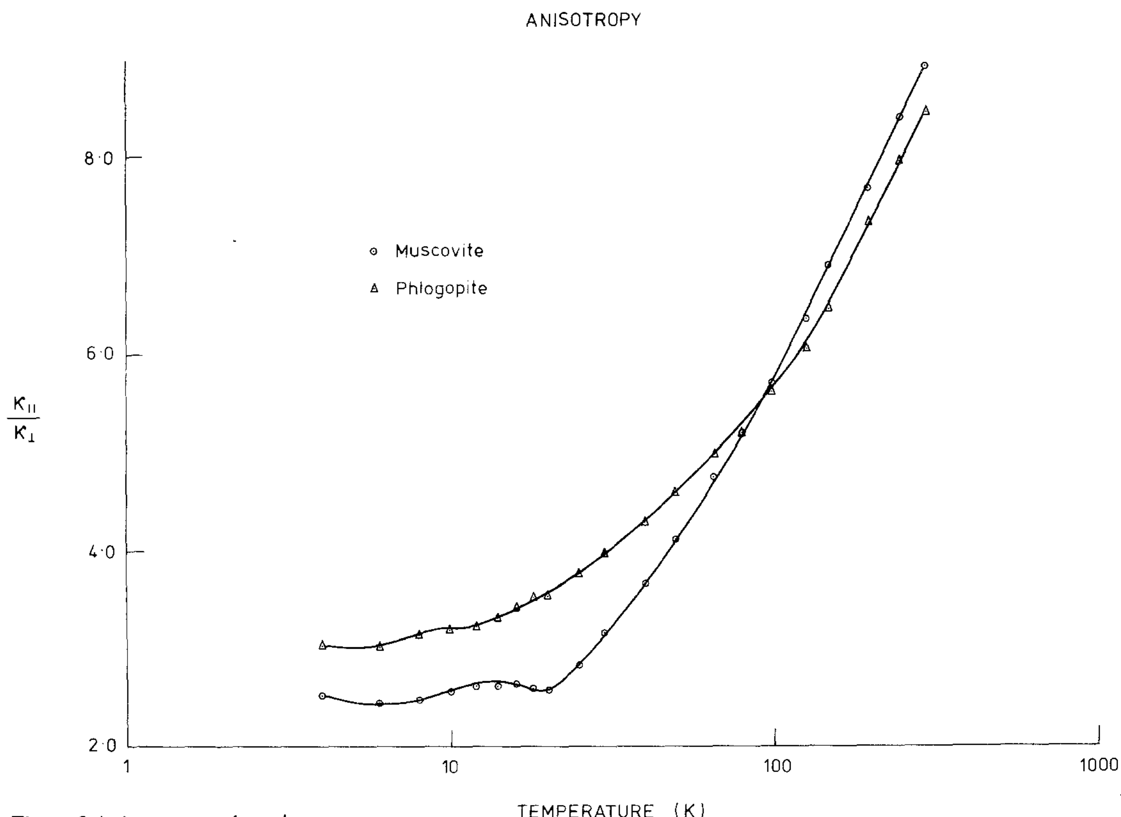

Figure 3 Anisotropy ratio $\kappa_{\parallel}/\kappa_{\perp}$

TABLE I

Parameter	Longitudinal Muscovite	Phlogopite	Transverse Muscovite	Phlogopite
κ_{max}(W m^{-1} K^{-1})	12.4	7.25	4.7	2.05
$T(\kappa_{max})$ (K)	13.5	17	14	15
κ_{300}	4.05	3.7	0.46	0.44
slope $< T_{max}$ (6 K)	1.25	1.23	1.25	1.27
slope $> T_{max}$ (25 K)	0.56	0.31	1.0	0.62
slope at 300 K	0.20	0.12	0.42	0.38
Density (kg m^{-3})	2.79×10^{-9}	2.72×10^{-9}	2.79×10^{-9}	2.72×10^{-9}

4. Discussion

Table II compares our results at 300 K with previously published work.

Considering that mica is a mineral with natural variations in composition, the values of κ obtained by us at 300 K are in reasonable agreement with other workers' results.

TABLE II Comparison of results at 300 K

Reference	Measured parameter	Value ($W m^{-1} K^{-1}$)
Present work	$\kappa_{\parallel}$ muscovite	4.0
[5]		3.35–3.96
Present work	$\kappa_{\parallel}$ phlogopite	3.7
[5]		2.89–2.91
[7]		5.0
Present work	$\kappa_{\perp}$ muscovite	0.46
[5]		0.545–0.585
[6]		0.68 ± 18%
Present work	$\kappa_{\perp}$ phlogopite	0.44
[8]		0.4–0.5
[5]		0.507–0.512
[6]		0.72

As noted by Powell and Griffiths [6] and Metsik [5] the amount of loading on the samples will affect the value of $\kappa_{\perp}$.

The two differently oriented longitudinal samples cut from the same piece of Indian muscovite gave the same results for $\kappa_{\parallel}$ as the Australian muscovite. Thus no dependence of $\kappa_{\parallel}$ on direction within the cleavage plane was found.

Anisotropy ratio values at 300 K of about 8 are higher than those reported by Metsik (Muscovite 6.75 to 6.25 and phlogopite 5.7). Earlier measurements by Jannettaz [4] gave values for unspecified micas of about 2.3 to 2.5 (incorrectly printed in the Landolt-Bernstein Tables [14] as 5.71 to 6.14).

Figs. 1 and 2 show that the conductivity rises to a maximum as the temperature is lowered, as is usual with crystalline solids. However, only in the case of muscovite $\kappa_{\perp}$ does the slope approach a T^{-1} law near the peak. Near room temperature $\kappa_{\parallel}$ for both types of mica is nearly independent of temperature. It may be relevant that phlogopite passes through a phase transition at about 560 K (see Anikin [15]), which is reflected in a change of thermal expansion coefficient parallel to the cleavage planes [11].

All four curves in Figs. 1 and 2 peak at about the same temperature. The slope at a temperature of 8 K is about + 1.25 for all curves, which is less than the T^2 law which has been proposed for layered materials. This value is not conclusive since at a lower temperature the phlogopite $\kappa_{\perp}$ slope steepens to 1.68.
is not conclusive since at a lower temperature the phlogopite $\kappa_{\perp}$ slope steepens to 1.6 W m^{-1}.

The curves of anisotropy (Fig. 3) for muscovite and phlogopite show similar characteristics. $\kappa_{\parallel}$ is the dominant component throughout the temperature range covered. This is to be expected because of the stronger forces between atoms within the layers than between adjacent layers. Presumably the shape of the graphs is related to the ratio of thermal expansion coefficients.

It is interesting to compare these results with work done on other layer-type materials such as pyrolytic graphite [16–18] which is electrically conductive, and boron nitride [19] which is insulating. In contrast to mica, both materials have an anistropy ratio at room temperature which is much larger than that of mica, of the order of 100 or more. Also, although a peak has not yet been found at low temperature in $\kappa_{\perp}$ of either material, it is evidently at a much lower temperature than the corresponding $\kappa_{\parallel}$ peak. Unfortunately no data exist for mica on acoustic wave velocities or phonon dispersion.

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