Long-wavelength phonons in GaTe

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(Received 24 July 1978)

The long-wavelength vibrational modes of monoclinic GaTe have been investigated by Raman scattering and far-infrared absorption and reflection. The energies of 14 of the expected 18 Raman-active modes have been measured and their symmetries identified. Ten of the 15 predicted infrared-active modes have been found in the infrared spectra. A comparison of the Raman and infrared results has not provided conclusive evidence concerning the existence of conjugate modes in GaTe, and possible reasons are discussed. The results are also compared to previous work and several differences are noted and discussed in detail.

I. INTRODUCTION

In recent years a great deal of interest has been focused on the semiconducting IV-VI layered compounds GaSe, GaS, and GaTe. This interest has arisen partly because of the approximate two-dimensional nature of the compounds, and partly because of possible technical applications. GaTe is a typical layer structure in that it exhibits a characteristic easy cleavage in the plane of the layers as a result of the very weak bonding between layers. The intralayer structure of GaTe, however, is quite different from that of GaSe and GaS. In the latter two compounds, each layer is built up four planes of atoms in the sequence Se-Ga-Ga-Se.[1] In GaTe, portions of an individual layer consist of four planes of atoms extending indefinitely in the direction of the crystal b axis (Fig. 1).[1] These portions are connected by another Te-Ga-Ga-Te series in which the Ga–Ga bonds are approximately at right angles to the other Ga–Ga bonds. As a consequence the crystal structure of GaTe is considerably more complex than the structure of GaSe and GaS. Presumably because of its relatively complicated monoclinic structure, GaTe has to date attracted far less attention than GaS and GaSe.

A number of workers,[2–9] however, have carried out measurements of the optical constants of GaTe, and the electrical properties have been the subject of a few investigations.[10–12] To the best of the authors' knowledge, the vibrational properties of GaTe have been the subject of a single recent investigation in which Cerdeira *et al*,[13] have reported on Raman-scattering experiments on the system $GaSe_{1-x}Te_x$ with $0 \leq x \leq 1$. This paper presents the results of Raman scattering and far-infrared absorption and reflectivity experiments carried out on GaTe. The Raman spectra were excited with the 1064.2-nm line of a YAlG:Nd^{3+} laser and the 514.5- and 488.0-nm lines of an argon laser. GaTe is a semiconductor with a room-temperature band edge[2] at approximately 1.65 eV, and is therefore transparent to the YAlG laser frequency (1.165 eV). Consequently, spectra are obtained that are unaffected by surface and resonant effects, and these spectra can be compared to the argon excited spectra.

Fourteen of the 18 predicted Raman-active modes have been observed and their symmetry identified. Ten of the possible 15 infrared-active modes have been observed in the absorption and reflectivity spectra. Several discrepancies occur when our results are compared to those of Cerdeira *et al.*[13] In particular, the mode assignments made in this work are quite different than those arrived at previously.[13] In addition, Cerdeira *et al.*, interpreted their results in terms of conjugate modes or Davydov splittings, whereas in the present paper, arguments are presented that suggest that

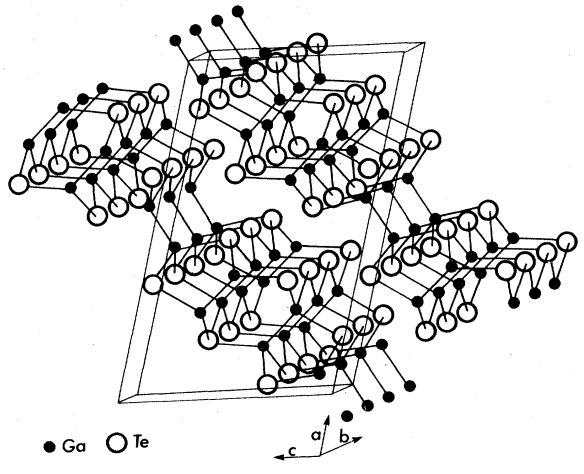

FIG. 1. Crystal structure of GaTe [after Pearson (Ref. 1)].

conjugate modes may not be present in GaTe.

A. Crystal structure

Single crystals of GaTe were grown in our laboratories using a vertical Bridgman technique, and were oriented using Laue x-ray reflection patterns to ±2°.

The crystal structure of GaTe was found to be monoclinic by both Hahn[14] and Schubert *et al.*,[15] but they arrived at different lattice parameters for the structure. Bryden[16] appears to have carried out the most detailed investigation of the structure, and he assigned the crystal symmetry to the $C_{2/m}$ (C_{2h}^3) space group. The lattice parameters found were in good agreement with those found by Schubert *et al.*[15] Dr. F.W.B. Einstein of the Chemistry Department at Simon Fraser University carried out some x-ray measurements on our crystals using a Buerger precession camera, and his observations were consistent with the structure proposed by Bryden.

Semiletov and Vlasov,[17] on the other hand, assigned GaTe to the $P2_1$ (C_2^2) space group on the basis of electron diffraction measurements. Their symmetry assignment, however, was tentative and in this work it will be assumed that GaTe crystallizes with $C_{2/m}$ symmetry. This decision is supported by the results obtained by Einstein at Simon Fraser University and conclusions reached by other workers.[18,19]

The crystallographic unit cell proposed by Bryden and Pearson (Fig. 1) contains a total of 12 molecular units. The primitive cell, however, from which the number of vibrational modes is determined, contains only six molecular units. The atoms in adjacent layers are symmetry related by the translational symmetry elements of the space group and hence the point group symmetry elements of an individual layer are identical to those of the crystal. These symmetry elements are those of the point group $C_{2/m}$.

B. Normal modes of vibration

GaTe has six molecular units in the primitive unit cell and thus 36 normal modes of vibration are expected for any particular wave vector $\vec{k}$. The symmetry of these modes can be found using the correlation method as outlined by Fateley *et al.*[20-22] In GaTe all the atoms are located at sites having C_s symmetry. Correlating this site symmetry with the factor group of the crystal (C_{2h}), one finds that at $\vec{k}=0$ the modes can be represented by the irreducible representations

$$\Gamma \equiv 12A_g + 6B_g + 6A_u + 12B_u .$$

All the A_g and B_g modes are Raman active,[23] and there should thus be 18 distinct Raman-active modes at the zone center. The acoustic modes are $A_u + 2B_u$ and the remaining $5A_u + 10B_u$ modes are infrared active.

The polarizability tensors for the A_g and B_g modes given by Loudon[23] are referenced to a Cartesian x, y, z coordinate system (x_1, x_2, x_3 set of Nye).[24] In this work the y axis is taken parallel to the symmetry b axis of the crystal, z is perpendicular to the layers, and x is in the plane of the layers.

II. EXPERIMENTAL

A. Raman scattering

A standard right-angle scattering geometry was used and spectra were obtained corresponding to all elements of the polarizability tensor. Spectra were taken at room temperature and at approximately 80 K by mounting the sample on the cold finger of a liquid-nitrogen-cooled Dewar. The scattered light was collected and analyzed with a Spex 1401 double monochromator and a photon counting system. For spectra excited with the 1064.2-nm Nd^{3+} line an ITT FW-118 photomultiplier was used, and for the argon-ion laser excited spectra, the scattered light was detected with an ITT FW-130 tube. To obtain spectra close to an Ar exciting line, a Spex third monochromator was incorporated into the system.

GaTe is a biaxial crystal, and to avoid depolarization effects due to birefringence, one should use a scattering geometry referenced to the optical axes of the crystal.[25] In addition, the collection optics should provide as small a collection angle as possible. The optical axes of GaTe, however, are not known and thus in this work all spectra are defined with respect to the Cartesian axes x, y, z defined previously.

A standard right-angle scattering geometry was used throughout the course of this work. It was found that spectra obtained with the incident light perpendicular to the layers were essentially depolarized, while spectra taken with incident light from the YAlG laser in the plane of the layers were highly polarized. The depolarization of the spectra obtained from surfaces perpendicular to the layers is due to the difficulty encountered in preparing high-quality surfaces perpendicular to the layers. It was also found that the degree of polarization present in the spectra was essentially independent of the speed of the collection optics.

From this experience it was concluded that surface quality was the dominant factor in determining

the depolarization of the spectra and that the collection angle was relatively unimportant. Consequently, the assigned mode symmetries were determined from spectra obtained from freshly cleaved surfaces and with the exciting light close to, and in the plane of, a surface parallel to the layers. The latter precaution was taken in an attempt to minimize birefringent effects. Spectra were also obtained from surfaces cut perpendicular to the layers, but these spectra were used only to identify any lines not present in the previous geometries. The above remarks refer to spectra taken with the YAlG laser; all spectra obtained with the argon-ion laser were found to be quite depolarized.

B. Infrared absorption and reflectivity

The far-infrared spectroscopic measurements carried out at Simon Fraser utilized a modified Beckman/RIIC FS-720 evacuated Michelson interferometer in conjunction with a germanium bolometer detector operating at 0.3 K. The resultant interferograms were Fourier transformed in the laboratory on a Hewlett-Packard minicomputer, and the ratio between sample and reference signals formed digitally.

The transmission measurements were made on thin single-crystal samples in a thermally isolated section of the detector cryostat. They were maintained at 4.2 K by thermal contact with an external ^{4}He bath.

Reflection measurements were made on freshly cleaved single crystals at room temperature. They were contained in a separate evacuated chamber placed between the interferometer and the detector cryostat. The angle of incidence was approximately 15°.

III. RESULTS AND DISCUSSION

A. Raman spectra excited with the YAlG:Nd laser

Examples of room-temperature spectra obtained with the YAlG:Nd laser are shown in Fig. 2(a) and 2(b). The numbered features in the figure correspond to the Raman-active modes, and their frequency and assigned symmetry character are listed in Table I. Spectra were taken for many scattering geometries and results were obtained corresponding to each element of the polarizability tensors. No modes, other than those present in Fig. 2, were found in the other scattering geometries, however. Thus of the 18 predicted Raman-active modes, 14 have been observed and identified. Spectra obtained at 80 K were very similar to those obtained at room temperature, except that the modes were shifted by approximately 1% to higher energies.

TABLE I. Measured frequency and assigned symmetry of the Raman-active modes in GaTe from Figs. 2(a) and 2(b). All values are accurate to ±2 cm^{-1}. The last column lists the frequencies observed by Cerdeira *et al.*[13] The bracketed symmetry assignments should be considered tentative.

Feature number	Energy (cm^{-1})	Assigned symmetry	Cerdeira (Ref. 13)
1	41	A_g	
			47
2	52	A_g	
3	58	B_g	57
			62
4	67	A_g	
5	76	A_g	
6	110	A_g	
7	115	A_g	
			128
			132
			143
8	155	(A_g)	
9	164	B_g	
10	170	B_g	169
11	178	(A_g)	178
12	208	A_g	
13	271	A_g	
14	284	A_g	

B. Raman spectra excited with the argon-ion laser

The Raman spectra obtained with the argon laser were of two quite different types. Figure 3 shows a spectrum obtained with the sample at 80 K and with about 100 mW of exciting power. As can be seen, this spectrum is similar to those obtained using the YAlG laser. Figure 4, however, shows a very different spectrum that was obtained with the sample at room temperature and with approximately 500 mW of exciting power.

The spectrum shown in Fig. 4 is dominated by three features at approximately 60, 130, and 145 cm^{-1}. Despite an extensive search no evidence has been found in any of the YAlG spectra of any peaks in the frequency region from 120 to 145 cm^{-1}. If such modes are present in the YAlG spectra, they must be at least 3 orders of magnitude weaker than the feature at 116 cm^{-1}, for example.

The occurrence of spectra such as the one shown in Fig. 4 was very puzzling in view of the YAlG results, and an effort was made to determine the

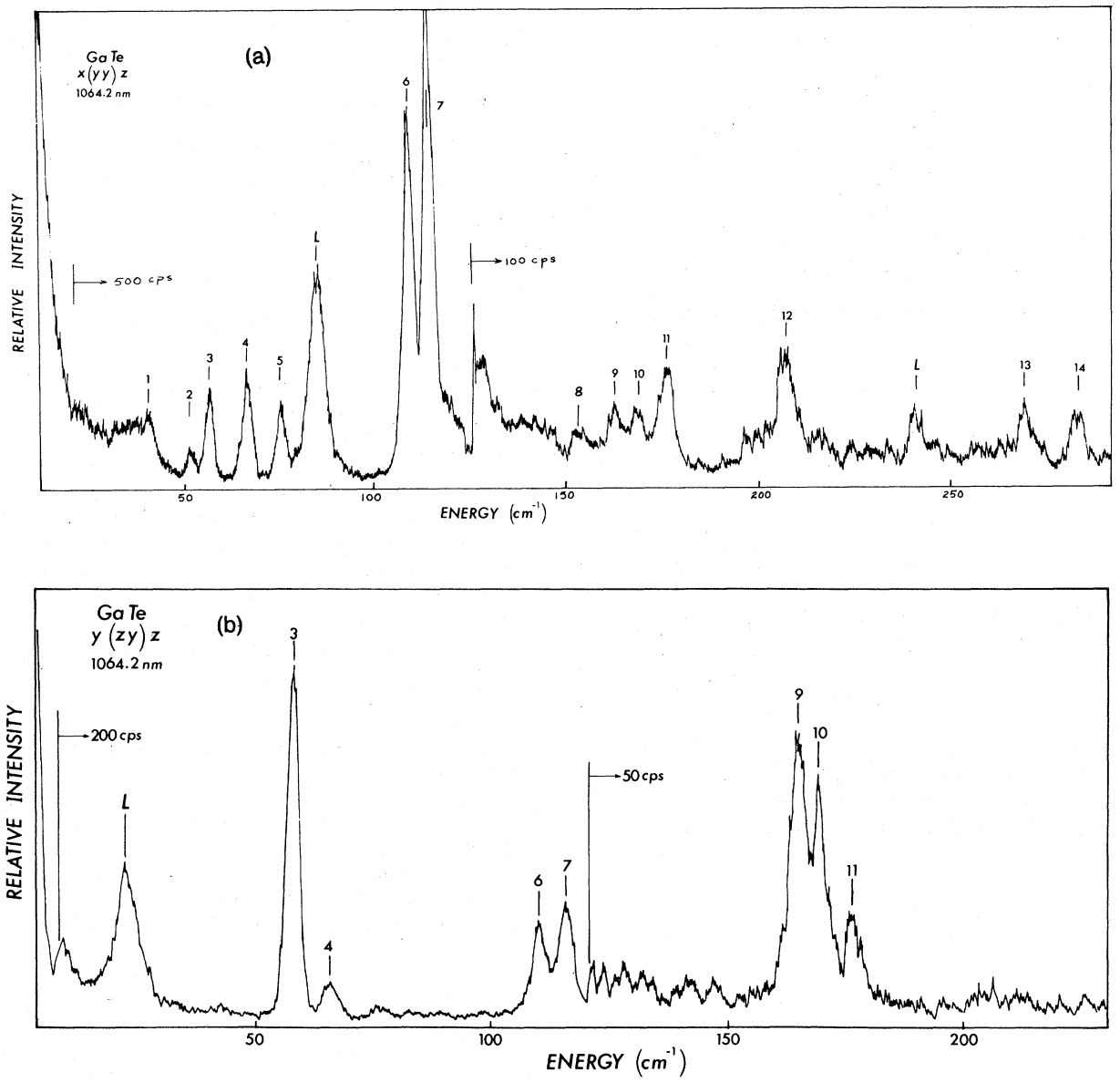

FIG. 2. Raman spectra of GaTe obtained at 300 K with the 1064.2-nm line of a YAlG: Nd^{3+} laser and 800-mW incident intensity.

origin of the dominant features at approximately 130 and 145 cm^{-1}. A systematic variation of the experimental conditions has enabled us to correlate the occurrence of spectra such as the one shown in Fig. 4 with high incident laser power (~500 mW) and/or tarnished surfaces. That is, such spectra were much more common from surfaces that were not freshly cleaved and were usually obtained with exciting powers greater than approximately 500 mW. In fact, in many cases, after observing such a spectrum, an investigation of the crystal revealed burn marks on the surface.

These observations are similar to those reported by Pine and Dresselhaus.[26] They found peaks at 60, 120, and 145 cm^{-1} in recording Raman spectra from tellurium, and attributed the origin of the peaks to the formation of TeO_2 caused by overheating.

As a result of our investigations and the observations of Pine and Dresselhaus, we have concluded that the prominent features in Fig. 4 do not correspond to vibrational modes of GaTe. It is as-

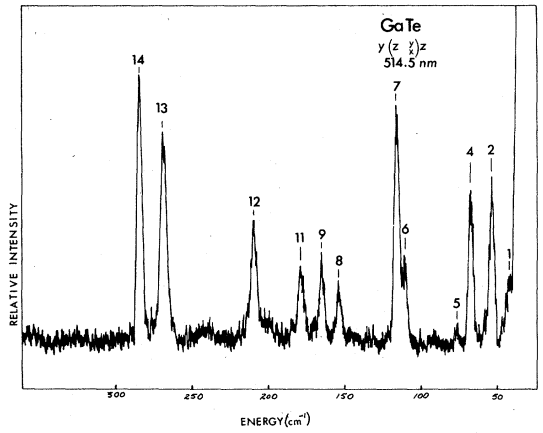

FIG. 3. Raman spectrum of GaTe obtained at 80 K with the 514.5-nm line of an argon-ion laser and 100-mW incident intensity.

sumed that these features arise from a different compound that is formed as a result of overheating or impurity adhesion on the crystal surface.

C. Infrared results

An infrared absorption spectrum is shown in Fig. 5, and a reflection spectrum in Fig. 6. The features indicated in the figures are tabulated in Table II. As can be seen, ten of the possible 15

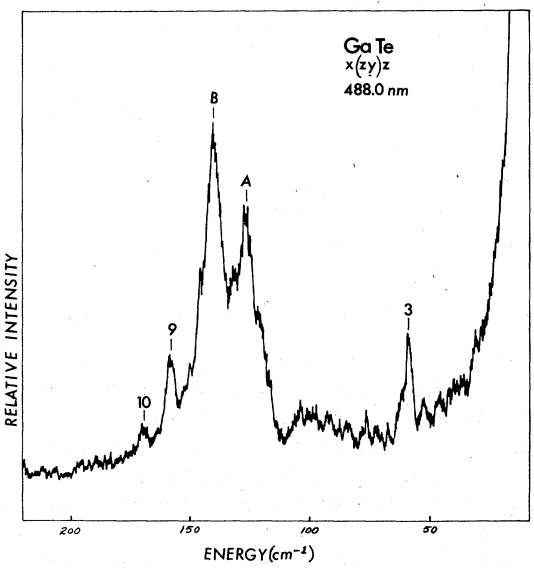

FIG. 4. Raman spectrum of GaTe obtained at 300 K with the 488.0-nm line of an argon-ion laser and 500-mW incident intensity.

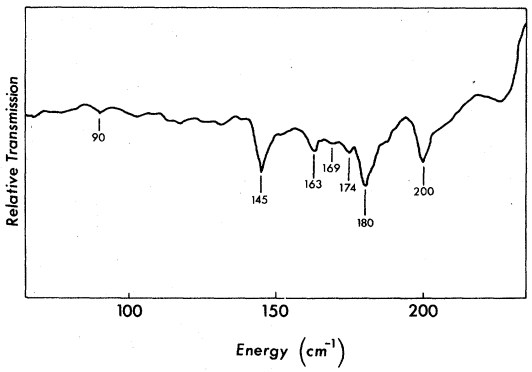

FIG. 5. Infrared absorption spectrum of GaTe obtained with the sample at 4 K and with the incident light traveling perpendicular to the plane of the layers.

infrared-active modes have been observed, all in the intermediate range of the Raman energies. Although some of the infrared modes have approximately the same energy as Raman modes, there is not a systematic correlation between the infrared and Raman energies. This result is discussed in more detail in Sec. IV.

IV. COMPARISON WITH PREVIOUS WORK

The Raman spectrum of GaTe has been investigated recently by Cerdeira *et al.*,[13] and their results are presented in the fourth column of Table I. As can be seen, the agreement between the two sets of results is poor. We have been unable

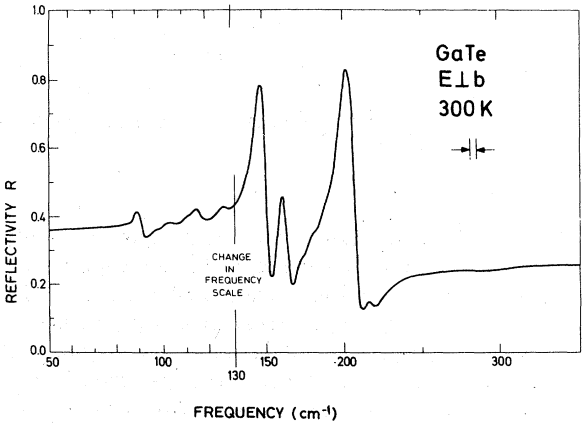

FIG. 6. Infrared reflection spectrum of GaTe obtained with the sample at 300 K and with E parallel to the crystal b axis.

TABLE II. Vibrational frequencies of GaTe obtained from the infrared absorption and reflectivity measurements. The brackets around the feature at 271 cm^{-1} indicate that it appeared weakly in the reflection spectra, and its identification must be considered tentative. All values are considered accurate to ±2 cm^{-1}. The feature at 185 cm^{-1} was observed with E perpendicular to the layers.

Reflection (cm^{-1})	Absorption (cm^{-1})
90	90
116	116
145	145
160	163
	169
	174
180	180
185*	
200	200
217	
(271)	

TABLE III. Comparison of the Raman and infrared frequencies observed in GaTe.

Raman (cm^{-1})	Infrared (cm^{-1})
41	...
52	...
58	...
67	...
76	...
...	90
110	...
115	116
...	145
155	...
164	163
170	169
...	174
178	180
...	185
...	200
208	217
271	(271)
284	...

to find the modes observed by Cerdeira *et al.* at 47, 62, 128, 132, and 143^{-1}. Three of these features, the peaks at 128, 132 and 143 cm^{-1}, correspond very closely to the major features of Fig. 4 and could perhaps be attributed to the same cause, namely, overheating of the samples.

Our results do not provide definitive evidence for the existence of conjugate modes, as suggested by Cerdeira *et al.*[13] Given the $C_{2/m}$ symmetry of GaTe and resultant even-odd dichotomy of the vibrational modes, the existence of conjugate modes would be revealed by a set of infrared-active modes essentially degenerate in energy with the set of Raman-active modes.[27,28] Although some of the infrared modes have frequencies almost equal to Raman frequencies (Table III), there are four modes that have no counterpart in the Raman spectra. In the absence of a systematic correlation between the infrared and Raman frequencies, it must be concluded that our results neither confirm nor negate the possible existence of conjugate modes in GaTe. On the other hand, one might not expect to see conjugate modes in GaTe. In GaTe the point-group symmetry elements of a single layer appear to be the same as those of the crystal as a whole, and both a single layer and the crystal as a whole are then characterized by $C_{2/m}$ point-group symmetry. This in turn implies that the even-odd dichotomy of the modes is present in a single layer and is not introduced by the coupling between layers. In this case one would not expect a degeneracy between the Raman and infrared modes and no rigid layer mode would be present. In support of this point of view it should be noted that, despite a careful search, we have not observed any modes between 10 and 40 cm^{-1}, the frequency region typically occupied by rigid layer modes.

In conclusion, however, the partial degeneracy between the sets of modes that we have observed in this work prohibits us from making a definitive statement on the existence or nonexistence of conjugate modes in GaTe.

ACKNOWLEDGMENTS

The authors would like to thank Prof. F. W. B. Einstein for carrying out x-ray measurements on GaTe and for several very helpful discussions. We would also like to thank Herr König of the Max Planck Institute for help in obtaining some of the infrared reflection spectra. We are also grateful to Prof. M. Cardona for a critical reading of the manuscript. Finally, the financial support of the National Research Council of Canada is gratefully acknowledged.

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