



# Auger-free luminescence due to interatomic p–d transition and self-trapped exciton luminescence in $\text{Rb}_2\text{ZnCl}_4$ crystals

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## ABSTRACT

It is reported that **Auger-free (AF) luminescence** appears with two bands at 4.5 and 6.3 eV in  $\text{Rb}_2\text{ZnCl}_4$ . This luminescence originates from a radiative transition of the Cl 3p valence electrons into the Zn 3d outermost-core holes. The present work is the first observation of AF luminescence due to interatomic p–d transitions in halide crystals. The appearance of two AF luminescence bands suggests the existence of two types of AF transitions following core hole creation. A largely Stokes-shifted luminescence band is also found to appear at 1.9 eV. This band has an excitation threshold at the fundamental absorption edge, and is ascribed to the radiative decay of a self-trapped exciton.

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## 1. Introduction

In ionic crystals in which the band-gap energy  $E_g$  is larger than the energy difference  $E_{VC}$  between the top of the valence band and that of the outermost-core band, a peculiar type of intrinsic luminescence called Auger-free (AF) luminescence [1,2] (cross-luminescence [3] or core–valence luminescence [4]) is emitted under core band excitation, in addition to the intrinsic luminescence from self-trapped excitons (STEs). This is because the valence electron excitation through a nonradiative Auger process is energetically impossible. The AF luminescence is practically useful for high-energy physics, medical inspections and so on [5], because it has a relatively high quantum efficiency and short decay time of the order of ns. Accordingly, extensive studies have been made on the optical properties of AF luminescence from the view point of applied science as well as basic science [6].

A considerable amount of information on AF and STE luminescence is available in simple halides AX such as CsCl and RbF [7–9], dihalides  $\text{BX}_2$  such as  $\text{BaF}_2$  [9–11] and trihalides  $\text{ABX}_3$  such as  $\text{CsCaCl}_3$  and  $\text{RbCaF}_3$  [12], where A is a monovalent cation, B a divalent cation and X a halogen anion. Such information, however, is very less in the case of tetrahalide  $\text{A}_2\text{BX}_4$ . Luminescence properties in  $\text{A}_2\text{BX}_4$  are worth studying in order to obtain a more

complete picture of AF luminescence, as well as that of STE luminescence, in halide crystals.

$\text{Cs}_2\text{ZnCl}_4$  and  $\text{Rb}_2\text{ZnCl}_4$  are typical crystals of  $\text{A}_2\text{BX}_4$  type. The crystal of  $\text{Cs}_2\text{ZnCl}_4$  ( $\text{Rb}_2\text{ZnCl}_4$ ) is composed of anionic  $\text{ZnCl}_4$  tetrahedra separated from each other and interstitial Cs (Rb) cations between them, as illustrated in Fig. 1 [13]. In the previous work [14], we have investigated optical properties of  $\text{Cs}_2\text{ZnCl}_4$  crystals with the use of synchrotron radiation as a light source, and observed AF luminescence resulting from a radiative transition between the Cl 3p valence band and the Cs 5p core band, without any signal of STE luminescence. The present study is a further extension to  $\text{Rb}_2\text{ZnCl}_4$  crystals. From reflection and X-ray photoelectron spectra, it is clarified that  $\text{Rb}_2\text{ZnCl}_4$  satisfies the condition for appearance of AF luminescence, that is,  $E_{VC} < E_g$ , similar to the case of  $\text{Cs}_2\text{ZnCl}_4$ . Existence of AF luminescence is actually confirmed from measurements of excitation spectra. **The AF luminescence in this crystal is ascribed to the interatomic p–d transition between the Cl 3p valence band and the Zn 3d core band.** A luminescence band arising from STEs is also found. This work reveals that an outermost-core hole, as well as a valence hole, induces considerable lattice relaxation within its lifetime in tetrahalides of  $\text{A}_2\text{BX}_4$  type.

## 2. Experiment

The crystals of  $\text{Rb}_2\text{ZnCl}_4$  were grown by slow evaporation from aqueous solutions of a molar ratio 2:1 of RbCl and  $\text{ZnCl}_2$ .

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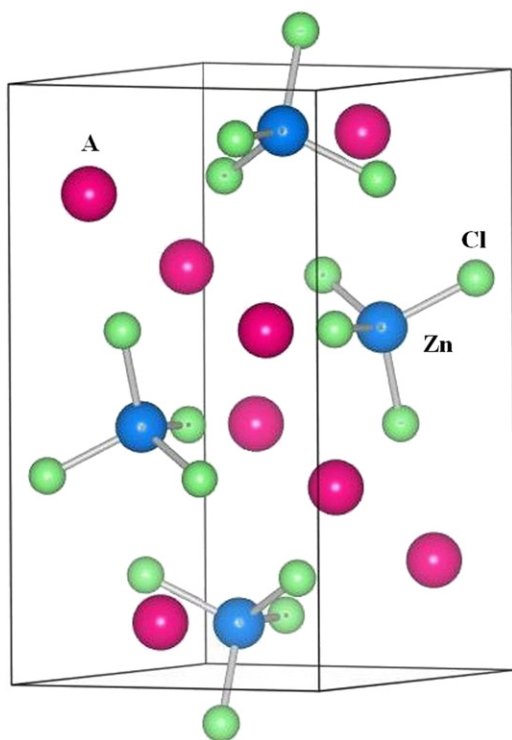


Fig. 1. Crystal structure of  $A_2ZnCl_4$  ( $A=Cs, Rb$ ).

The obtained crystals were colorless and transparent. By X-ray diffraction, their lattice parameters at room temperature were confirmed to be in good agreement with a crystal database of  $Rb_2ZnCl_4$ . The crystal was mechanically cleaved, and attached on the copper holder of a cryostat of liquid He flow-type. The sample chamber was evacuated to less than  $1.0 \times 10^{-6}$  Pa. The sample temperature was controlled in the range 10–300 K by using a combination of a controller (SI Model 9650), a calibrated silicon diode sensor and an electric heater.

The measurements of reflection, emission and excitation spectra were performed at beamline 7B by using vacuum ultra-violet (VUV) light from synchrotron radiation of the UVSOR facility (Institute for Molecular Science, Okazaki) equipped with a 3 m normal incident monochromator with a gold-coated grating (groove density: 1200 lines/mm). The spectral resolution of this primary monochromator was better than 0.1 nm. Higher-order light from the monochromator was eliminated by inserting LiF or quartz plates between the sample and the light source. The intensities of incident and reflected light were measured with a photomultiplier with a glass window coated by sodium salicylate phosphor. Reflectivity spectra were obtained by dividing the reflected light intensity by the incident light intensity. Luminescence emitted from the sample surface was focused on the entrance slit of a grating monochromator (Acton SpectraPro 2300i, groove density: 150 lines/mm) by quartz lenses, and then detected by a photomultiplier (Hamamatsu R955) or a CCD detector (Roper Scientific 100EB-GI). The spectral resolution of the secondary monochromator was set to about 12 nm. In the luminescence measurement, we used appropriate filters in order to cut off the second order light from the grating. The emission spectra were corrected for the dispersion of the monochromator, i.e.  $\lambda^2$  correction, and for the spectral sensitivity of the detection system. This spectral sensitivity was determined in the region longer than 300 nm by using a calibrated tungsten lamp and in the region shorter than 300 nm by the spectral radiance of synchrotron light derived from a comparison with the constant

yield of sodium salicylate. The excitation spectra were corrected for the intensity distribution of the incident light measured using sodium salicylate.

X-ray photoelectron spectroscopy (XPS) was performed at room temperature using an ESCA spectrometer (ULVAC-PHI 5600), with an excitation source of Al anode ( $K\alpha$ : 1486.6 eV). An electron flood gun was employed to compensate for sample charging under X-ray irradiation. The energy resolution was about 0.5 eV. The base pressure in sample chamber was less than  $6.0 \times 10^{-7}$  Pa.

### 3. Results and discussion

The reflection spectrum of  $Rb_2ZnCl_4$  at 10 K in the range 5–30 eV is shown in Fig. 2. Two sharp bands denoted by  $E_1$  and  $E_2$  are peaked at 7.27 and 7.84 eV, respectively. The lowest band  $E_1$  is naturally attributed to the  $n=1$  exciton transition. By calculating the second-energy-derivative spectrum, this band turned out to be composed of two bands at 7.27 and 7.46 eV, as indicated by two vertical lines in the inset of Fig. 2. Their energy difference is 0.19 eV. Since this value is comparable with the spin-orbit splitting of the valence band in alkali chlorides [15], the two bands are assigned to the halogen doublet related to optical transitions from the Cl 3p valence band to the Rb 5s conduction band, that is, exciton absorption of  $j=3/2$  and  $1/2$ . On the other hand, the second band  $E_2$  may be assigned to the  $n=2$  exciton transition. If this is the case, the value of  $E_g$  is estimated to be 8.03 eV by assuming that the exciton energy levels are hydrogen-like.

Three sharp bands  $P_1$ ,  $P_2$  and  $P_3$  are situated at 16.47, 16.65 and 17.53 eV, respectively. These bands are observed in the same energy region as those of the core exciton bands in RbCl [15]. Furthermore, the difference between the weighted mean energy of  $P_1$  and  $P_2$  peaks and the energy of the  $P_3$  peak is nearly 0.97 eV, which is nearly equal to the spin-orbit splitting of the Rb 4p core level in RbCl [15]. Therefore, it is reasonable to assign the three peaks to the core exciton absorptions due to Rb 4p→5s transitions. The 4p state splits into the  $4p_{3/2}$  and  $4p_{1/2}$  states by spin-orbit interaction. Owing to the crystal field, the  $4p_{3/2}$  state further splits into the  $4p_{3/2}(p_x)$  and  $4p_{3/2}(p_y)$  sublevels. We thus attribute the  $P_1$  and  $P_2$  bands to the transitions from the Rb  $4p_{3/2}(p_x)$  and  $4p_{3/2}(p_y)$  states, respectively, and the  $P_3$  band to that from the Rb  $4p_{1/2}(p_z)$  state.

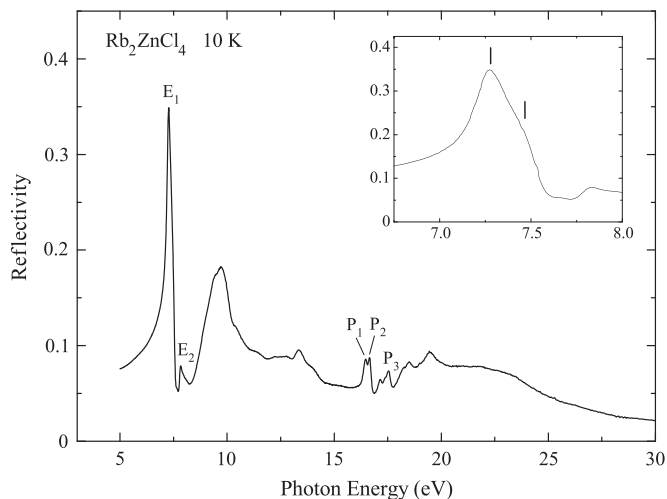


Fig. 2. Reflection spectrum at 10 K in the range 5–30 eV. The inset shows the reflection spectrum in an expanded scale in the 6.5–8.0 eV range.

Fig. 3 shows the XPS spectrum, in which the onset of valence band is taken as the origin of binding energy. Four bands are peaked at 9.0, 11.7, 13.9 and 27.6 eV below the top of the valence band composed of the Cl 3p states. The spectrum of Fig. 3 is very similar to that of RbCl [16], except for appearance of a band at 9.0 eV. On the basis of this similarity, we attribute the 11.7, 13.9 and 27.6 eV bands to the Rb 4p, Cl 3s and Rb 4s states, respectively. The 9.0 eV band is likely assigned to the Zn 3d state, because of a good agreement with the binding energy of the Zn 3d state in a  $\text{ZnCl}_2$  molecule [17]. A schematic energy-level diagram of  $\text{Rb}_2\text{ZnCl}_4$  determined from XPS measurement is presented in the inset of Fig. 3.

From the above result of XPS and the previous study on  $\text{Cs}_2\text{ZnCl}_4$  [14], it is interesting to point out that the Zn 3d state in  $\text{Rb}_2\text{ZnCl}_4$  is located above the Rb 4p state, while that in  $\text{Cs}_2\text{ZnCl}_4$  is located at almost the same energy position as that of the Cs 5p state. In order to check whether AF luminescence is observable in  $\text{Rb}_2\text{ZnCl}_4$ , the value of  $E_{\text{VC}}$  between the top of the Cl 3p valence band and that of the Zn 3d outermost-core band is estimated by referring to the XPS spectrum of Fig. 3. The obtained value is  $6.4 \pm 0.5$  eV, in which the uncertainty comes from insufficient resolution of XPS measurements. It should be stressed that the value of  $E_{\text{VC}}$  is smaller than  $E_{\text{g}}$  (8.03 eV), even if the experimental errors of each value are most severely evaluated. This result lets us expect that AF luminescence appears in  $\text{Rb}_2\text{ZnCl}_4$  when an outermost-core hole is created in the Zn 3d band by photo-excitation.

Emission spectra of  $\text{Rb}_2\text{ZnCl}_4$  were measured at 10 K under core band excitation with 21.4 eV photons. The result is shown by curve 1 (black solid line) in Fig. 4, whereas curves 2 (red dotted line) and 3 (blue broken line) represent the emission spectra obtained under the excitation with 10.3 and 6.5 eV photons, respectively. Curve 1 consists of five bands peaking at 1.9, 2.8, 3.8, 4.5 and 6.3 eV. This spectrum is in good agreement with that observed under X-ray excitation by Martin et al. [18], except for the 6.3 eV band. They have attributed two main bands at 1.9 and 4.5 eV to intrinsic electron–hole recombination, that is, recombination of electrons with self-trapped holes. However, no experimental evidence for this has been given until now. It should be noticed that the 4.5 and 6.3 eV bands are not stimulated under excitation with 10.3 and 6.5 eV photons, as shown by curves 2 and 3. Furthermore one may see that the 1.9 eV band is excited by 10.3 eV photons, but not by 6.5 eV photons. The 2.8 and 3.8 eV bands are intensely stimulated under excitation with 6.5 eV photons.

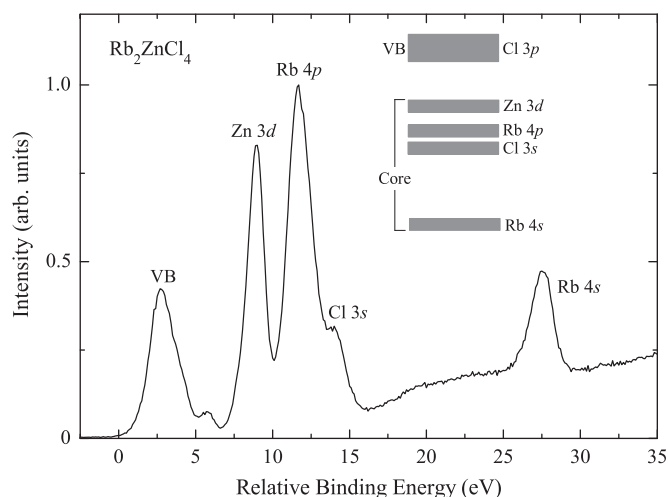


Fig. 3. X-ray photoelectron spectrum, in which the binding energy is given relative to the top of the valence band. The inset shows schematic energy-level diagram determined from XPS measurement.

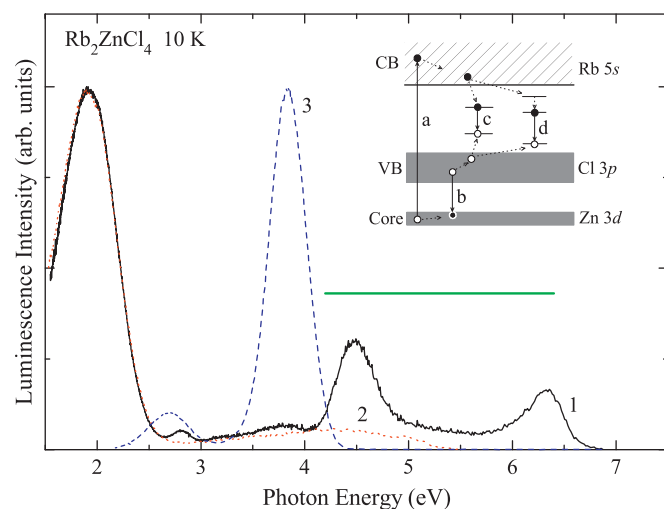


Fig. 4. Luminescence spectrum measured at 10 K under excitation with 21.4 eV (1: black solid line), 10.3 eV (2: red dotted line) and 6.8 eV (3: blue broken line) photons. Each spectrum is normalized at the maximum. See text for the green line. The inset illustrates possible transition processes under outermost-core level excitation. (a) optical absorption, (b) AF luminescence, (c) STE luminescence, and (d) defect luminescence. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

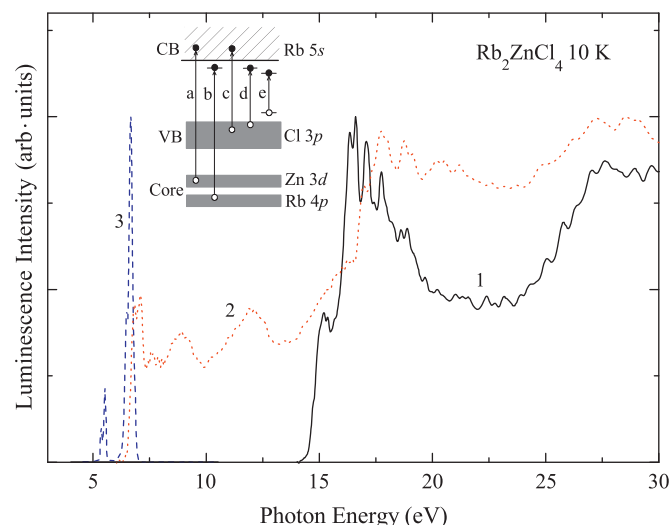


Fig. 5. Excitation spectrum for 4.5 eV (1: black solid line), 3.8 eV (2: red dotted line) and 1.9 eV (3: blue broken line) bands measured at 10 K. Each spectrum is normalized at the maximum. The inset illustrates five kinds of excitation processes. (a) Zn 3d core-to-conduction band, (b) Rb 4p core exciton, (c) valence-to-conduction band, (d) valence exciton, and (e) imperfection. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Excitation spectra for the five emission bands were measured in the range 4–30 eV at 10 K. The results for 4.5, 3.8 and 1.9 eV bands are shown by curves 1 (black solid line), 2 (red dotted line) and 3 (blue broken line) in Fig. 5, respectively. The results for 2.8 and 6.3 eV bands were almost the same as those for 3.8 and 4.5 eV bands, respectively. The excitation spectrum for the 4.5 eV band sharply rises at around 14.0 eV. Its intensity exhibits a peak at 15.2 eV and increases above 16 eV which corresponds to the onset of the core exciton band  $P_1$  due to transitions from the Rb 4p state. The dips of the excitation spectrum in the 16–18 eV range coincide with the peaks of the reflection spectrum. It is noteworthy that the threshold energy (14.0 eV) of the 4.5 eV band agrees well with the energy required to excite AF luminescence,

that is, the transition energy from the Zn 3d outermost-core band to the Rb 5s conduction band;  $E_g + E_{VC} \approx 14.4$  eV. Therefore, the 4.5 and 6.3 eV bands are surely ascribed to radiative recombination of Cl 3p valence electrons with Zn 3d core holes, in contrast to the assignment in Ref. [18].

It is stressed that AF luminescence in  $\text{Rb}_2\text{ZnCl}_4$  is realized through an interatomic p–d transition. In AF materials found to date [6], the valence band is formed by the p states of halogen ions, whereas the outermost-core band is built up by the p states of metal ions. Therefore, previously observed AF luminescence is usually attributed to interatomic p–p transitions. The present work is the first observation of AF luminescence due to interatomic p–d transitions.

When the  $\text{Rb}_2\text{ZnCl}_4$  crystal was warmed, it was found that the AF luminescence begins to disappear at around 190 K and becomes very weak at room temperature, although the condition of  $E_{VC} < E_g$  is still fulfilled. The origin of this temperature dependence is under investigation, together with decay behaviors of AF luminescence.

If a hole created in an outermost-core band relaxes to the top of the band before it decays radiatively, and also if the effect of lattice relaxation is negligible (rigid band model), the photon energy of AF luminescence could be emitted in the range  $E_{VC} - \Delta E_v \leq h\nu \leq E_{VC}$ , where  $\Delta E_v$  is the valence band width. We get  $\Delta E_v = 2.2 \pm 0.5$  eV from the XPS spectrum of Fig. 3. The energy range thus estimated is  $4.2 \text{ eV} \leq h\nu \leq 6.4 \text{ eV}$ , where the experimental uncertainty is  $\pm 1.0$  eV. This range is indicated by a green bar in Fig. 4. It appears that the 4.5 and 6.3 eV bands are almost situated in this range. The existence of two AF luminescence bands suggests that there are two types of AF transitions under core hole creation in  $\text{Rb}_2\text{ZnCl}_4$ . Such a suggestion would be supported by a theoretical consideration of AF luminescence by Fukaya et al. [19]. They assume that an outermost-core hole self-traps by inducing lattice deformation around itself. From the arguments in Ref. [19], we consider that the high-energy band at 6.3 eV comes from the AF transition of a self-trapped core hole to a localized state in the valence band due to an attractive potential of lattice deformation created in the initial state. The final state of the low-energy band at 4.5 eV, on the other hand, is an extended state in the valence band without lattice deformation.

As for the double-peaked structure of AF luminescence, cluster calculation by Bikmetov et al. [20] has shown that the number of AF luminescence bands is closely related to the coordination number of a cation on which a core hole is created. In their model, it is predicted that the density of state of the valence band also has a double-peaked structure. The valence XPS spectrum of  $\text{Rb}_2\text{ZnCl}_4$ , however, consists of a single band, although our energy resolution is insufficient. It seems that the model of Bikmetov et al. is not suitable for the present case. The spectral shape of AF luminescence is still an interesting subject for experimental and theoretical studies on inner-shell excitation.

As shown by curve 2 in Fig. 5, the excitation spectrum for the 1.9 eV band sharply rises at around 6.6 eV. Since this threshold coincides with the absorption edge of the  $n=1$  exciton, it is most likely that the 1.9 eV band arises from radiative decay of STEs. On the other hand, the 2.8 and 3.8 eV bands are efficiently stimulated in the low-energy side of the fundamental absorption, as shown by curve 3 in Fig. 5. These bands are supposedly related to some lattice imperfection. The 1.9 eV STE luminescence is quenched on increasing the temperature above 70 K, which is in good agreement with the observation by Martin et al. [18].

López and Martin [21] have found by means of electron paramagnetic resonance that a  $\text{Cl}_2^-$  molecular ion, a valence hole equally shared by two neighboring chlorine ions, is formed in  $\text{Rb}_2\text{ZnCl}_4$  X-irradiated at 77 K. As in the case of alkali halides, we think that an STE in  $\text{Rb}_2\text{ZnCl}_4$  is composed of a  $\text{Cl}_2^-$  ion and a bound electron. The 1.9 eV STE luminescence has a remarkably large Stokes shift beyond 5.0 eV relative to the lowest exciton absorption energy. This fact strongly suggests that, in  $\text{Rb}_2\text{ZnCl}_4$ , a hole created in the Cl 3p valence band induces a great deal of lattice deformation when it becomes self-trapped. The self-trapping of a valence hole onto a  $\text{Cl}_2^-$  ion would be reflected in the structural configuration of the STE, but it still remains unclear in the present study. Further experimental studies are very much required to clarify the STE configuration in tetrahalides of  $\text{A}_2\text{BX}_4$  type.

In summary, the AF and STE luminescence in  $\text{Rb}_2\text{ZnCl}_4$  were investigated with use of synchrotron radiation as a light source. Two AF luminescence bands were found at 4.5 and 6.3 eV, which originate from the interatomic p–d transitions between the Cl 3p valence band and the Zn 3d outermost-core band. The existence of two AF luminescence bands suggests that an outermost-core hole self-traps by inducing lattice deformation around itself. An STE luminescence band was also found at 1.9 eV. We suppose that the STE consists of a  $\text{Cl}_2^-$  ion and a bound electron, though its structural configuration is an open question.

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