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# Upconversion Luminescence in $\text{Nd}^{3+} : \text{LaCl}_3$ \*

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**Abstract** Blue and near violet upconversion luminescence originating from  ${}^4\text{D}_{3/2}$  and  ${}^2\text{G}_{9/2}$  levels in  $\text{Nd}^{3+} : \text{LaCl}_3$  can be induced upon excitation into  ${}^2\text{G}_{7/2} + {}^4\text{G}_{5/2}$  in the yellow region. Upconversion occurs via an energy transfer mechanism with or without excited-state absorption. Analysis of the upconversion transient of  ${}^4\text{D}_{3/2} \rightarrow {}^4\text{I}_{11/2}$  radiative transition at 12K leads to a rate constant  $w_{it} = 1468 \text{ s}^{-1}$  for the energy transfer step. The lifetimes of the main fluorescence levels of  $\text{Nd}^{3+} : \text{LaCl}_3$  and  $\text{NdCl}_3$  in the visible range were measured and the values are compared and discussed.

**Key words** Upconversion, Transfer rate, Lifetimes,  $\text{Nd}^{3+} : \text{LaCl}_3$  and  $\text{NdCl}_3$  crystals

## 1 Introduction

Among lanthanide ions  $\text{Nd}^{3+}$  is certainly the most thoroughly spectroscopically investigated.  $\text{Nd}^{3+}$  spectroscopy was in fact an early example of rare earth crystal spectra for which extensive quantum number assignments could be made<sup>[1]</sup>. The most satisfactory host for such study is  $\text{LaCl}_3$ , because of its rather high point-group symmetry ( $C_{3h}$ ), its rich fluorescence spectra favored by low vibration energies and the non-interference of superimposed vibronic spectra. Carlson and Dieke began their classic study on  $\text{Nd}^{3+} : \text{LaCl}_3$  in 1961 and supplied very good basis for the following researches<sup>[2]</sup>. Crosswhite and Crosswhite in 1976 published new results about  $\text{Nd}^{3+} : \text{LaCl}_3$ <sup>[3]</sup>. By using 20 adjustable parameters in a Hamiltonian containing many operators, they fitted 101 energy levels of  $\text{Nd}^{3+} : \text{LaCl}_3$ . Six years later, Rana *et al.* investigated Zeeman splitting of  $\text{Nd}^{3+}$  levels in  $\text{LaCl}_3$ <sup>[4]</sup>. Since this last work, energy levels of  $\text{Nd}^{3+}$  in  $\text{LaCl}_3$  were thought to be studied completely.

Full knowledge of the energy levels of  $\text{Nd}^{3+} : \text{LaCl}_3$  is a good basis for upconversion study. Existing data for upconversion of  $\text{Nd}^{3+}$  are only concerning infrared to visible process<sup>[5,6]</sup>. In this paper, we took this advantage to study the yellow to blue and near violet upconversion phenomena, spectrally and in function of the temperature. The relevant upconversion mechanisms were identified and the rate constant determined. In addition, the lifetimes of the main radiative levels of  $\text{Nd}^{3+}$ :

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$\text{LaCl}_3$  and  $\text{NdCl}_3$  in the visible range were measured and discussed.

## 2 Experiment

The sample  $\text{Nd}_{0.01}:\text{LaCl}_3$  grown from the melt by the Bridgman method was mounted in a quartz tube sealed under 60 kPa of He and placed in a circulating liquid - helium optical cryostat (OXFORD International). The excitation source is a dye laser pumped by the second harmonic of YAG:Nd laser (Quantel 20W) with a repetition rate of 30Hz and a duration of 10ns. The fluorescent emission was analyzed with a Jobin-Yvon HR-1000 monochromator and detected by a Hamamatsu R374 photomultiplier. The output was analyzed by a Stanford SR-510 lock-in amplifier and stored in computer memories. The luminescence decay curve was measured by a Lecroy 9350M oscilloscope (500MHz) interfaced with a computer.

## 3 Results

A typical observation of the upconverted fluorescence is shown in figure 1. The laser pumping at 582.6nm populates both  ${}^2G_{7/2} + {}^4G_{5/2}$  levels and generates up converted fluorescence from  ${}^4D_{3/2}$  and  ${}^2G_{9/2}$  levels. Their luminescence intensity dependence upon laser power is quadratic, indicating a two-photon process to populate the emitting levels. The excitation spectrum of the upconverted  ${}^4D_{3/2} \rightarrow {}^4I_{11/2}$  luminescence at 385.2nm ( $25961\text{cm}^{-1}$ ) in  $\text{Nd}^{3+}:\text{LaCl}_3$  is shown in figure 2. For comparison, the excitation spectrum of the Stokes emission from  ${}^4G_{5/2}$  is given in the lower part of the figure. The two excitation spectra are quite similar, but there exists two pronounced differences.

The first one is concerning the strongest excitation peak at 582.6nm ( $17164\text{cm}^{-1}$ ) which is attributed to transition between Stark levels of  ${}^4I_{9/2}(5/2) \rightarrow {}^2G_{7/2}(3/2)$ <sup>[4]</sup>. This peak is much narrower in excitation spectrum of upconverted luminescence than for normal downgraded luminescence. The second difference is for peaks at 578.2 and 580.3nm; whose relative intensity changes upon excitation modes, showing that the direct luminescence is more efficient than the

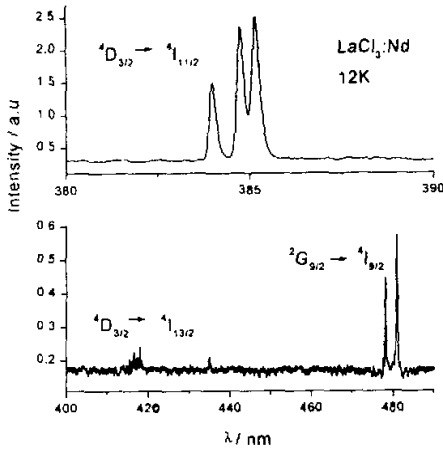


Fig.1 Emission spectrum of  $\text{Nd}^{3+}:\text{LaCl}_3$  at 12K using excitation at 582.6nm

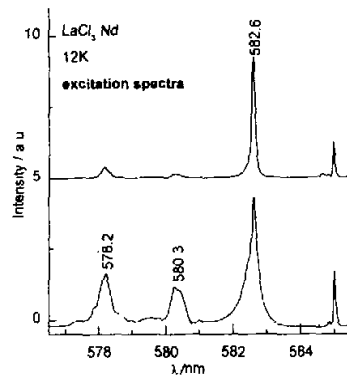


Fig.2 Excitation spectrum of  $\text{Nd}^{3+}:\text{LaCl}_3$  at 12K for  ${}^4D_{3/2} \rightarrow {}^4I_{11/2}$  transition at 385.2nm

upconversion process.

Figure 3 shows the intensity decay profiles of  ${}^4D_{3/2}$ ,  ${}^2G_{9/2}$  and  ${}^4G_{5/2}$  emissions after pulse selective excitation of each level at 12K. The plot reveals that they are all pure single exponential with lifetimes of 10.3, 87.6 and 29.2  $\mu\text{s}$  respectively. For decay measurement of the  ${}^4G_{5/2}$  emission intensity, the laser was set at 578.2nm with a very low input power to avoid upconversion phenomena.

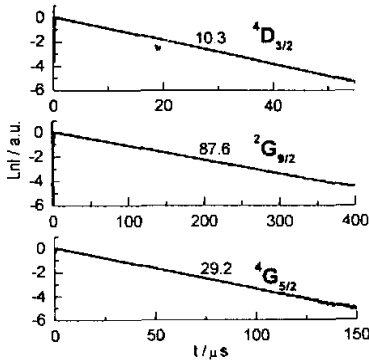


Fig. 3 Luminescence decay after resonant excitation to  ${}^4D_{3/2}$ ,  ${}^2G_{9/2}$  and  ${}^4G_{5/2}$  of  $\text{Nd}^{3+} : \text{LaCl}_3$  at 12K respectively

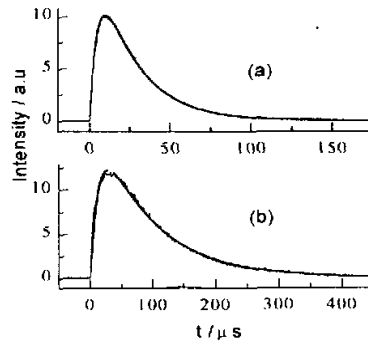


Fig. 4 Upconversion - luminescence transients of  ${}^4D_{3/2} \rightarrow {}^4I_{11/2}$  (a) and  ${}^2G_{9/2} \rightarrow {}^4I_{9/2}$  (b) after  ${}^2G_{7/2} + {}^4G_{3/2}$  excitation (582.6nm) of  $\text{Nd}^{3+} : \text{LaCl}_3$  at 12K

The upconverted luminescence transients of  ${}^4D_{3/2}$ ,  ${}^2G_{9/2}$  lowest Stark level obtained after pulsed excitation of  ${}^2G_{7/2} + {}^4G_{5/2}$  levels in  $\text{Nd}^{3+} : \text{LaCl}_3$  at 12K are shown in figures 4(a) and (b) respectively. The luminescence intensity is seen to slowly build up after the excitation pulse. An analysis in terms of rise and decay times, which will be discussed in the next section, yielded the following results: 4.5 and 24.6  $\mu\text{s}$  for  ${}^4D_{3/2}$ , 12.9 and 89.6  $\mu\text{s}$  for  ${}^2G_{9/2}$ .

The lifetimes of main fluorescent levels of  $\text{Nd}^{3+} : \text{LaCl}_3$  and  $\text{NdCl}_3$  determined from luminescence time - dependent measurements are listed in table 1. The values for  ${}^4D_{3/2}$  and  ${}^4G_{5/2}$  levels in  $\text{Nd}^{3+} : \text{LaCl}_3$  at 12K are the same as the ones given by Barasch and Dieke<sup>[7]</sup>, while for  ${}^2G_{9/2}$  and  ${}^4G_{7/2}$  levels, the results are in somewhat different, especially for  ${}^2G_{9/2}$  level providing a much larger value 87.6  $\mu\text{s}$ . The lifetimes for  $\text{Nd}^{3+}$  levels in  $\text{NdCl}_3$  shortened more than two orders compared with  $\text{Nd}^{3+}$  diluted in  $\text{LaCl}_3$  due to efficient cross-relaxations in pure materials<sup>[8]</sup>. Comparison with former measurements is difficult because almost no data are available. The only value that we have found in literature is for  ${}^4G_{5/2}$  level at 4.2K which was reported to be less than 3  $\mu\text{s}$ <sup>[5]</sup>, consistently with our measurements. Whereas the lifetime of  ${}^4G_{5/2}$  in  $\text{Nd}^{3+} : \text{LaCl}_3$  is strongly temperature dependent - it decreases from 29.2  $\mu\text{s}$  at 12K to 10.2  $\mu\text{s}$  at room temperature - the value of the  ${}^4D_{3/2}$  lifetime is not significantly affected by the temperature. The lifetime dependence on temperature for different energy levels should be related to the energy gaps between electronic levels.

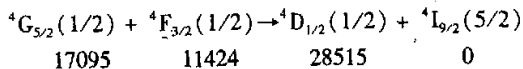
Table 1 Lifetimes of main luminescence energy levels of  $\text{Nd}^{3+}$  in  $\text{LaCl}_3$  and  $\text{NdCl}_3$  at room temperature (RT) and 12K

Level	$\text{LaCl}_3 : \text{Nd}$ lifetime / $\mu\text{s}$		$\text{NdCl}_3$ lifetime / $\mu\text{s}$	
	RT	12K	RT	12K
$^4\text{D}_{3/2}$	9.4	10.3	<0.01	0.052
$^2\text{G}_{9/2}$	-	87.6		
$^4\text{G}_{7/2}$	-	55.6		
$^4\text{G}_{5/2}$	10.2	29.2	~0.011	0.17

#### 4 Discussion

Basically, upconversion can occur by two different processes, excited - state absorption (ESA) and energy transfer between two partners (ETU)<sup>[9]</sup>. A distinction between the two mechanisms can often be made on the basis of energy arguments. Energy transfer process is more efficient when the exciting laser frequency is resonant with the ground - state absorption. Compared to energy transfer, the efficiency of an ESA upconversion process is determined by both the ground - state absorption and excited - state absorption cross sections. Therefore, efficient upconversion often occurs when the laser frequency is resonant with the second step, i. e. ESA. A clear distinction between ESA and ETU can be achieved by measuring their transients<sup>[10,11]</sup>. The former is characterized by an immediate decay just after excitation, while the latter one has an observable rise time after the laser pulse followed by luminescence decay. But if the both processes contribute to the same upconversion phenomena, we will expect a shorter rise time than that characterizing ETU process only.

As shown in figure 3,  $^4\text{G}_{5/2}$  level has a lifetime of  $29.2\mu\text{s}$  at 12K. This value was obtained by using a resonant excitation with a limited laser power in order to prevent upconversion phenomena. This is not the case shown in figure 1, where the laser power was not set low enough. However, the decay profile of  $^4\text{G}_{5/2}$  level at this high energy excitation condition remains single exponential but its decay time is no longer  $29.2\mu\text{s}$ , but a smaller value,  $28\mu\text{s}$ , was determined by fitting the curve (b) of figure 5. It should be pointed out that curves (a) and (b) in figure 5 are average results of 1000 times measurements, and giving an error less than 2%. In fact the figure clearly shows that curve (b) has a shorter lifetime. This change in lifetimes suggests that a new channel is opened and therefore the observed upconversion process is related to  $^4\text{G}_{5/2}$  level. From this statement, together with the well - established  $\text{Nd}^{3+}$  energy level scheme by Rana *et al.*<sup>[4]</sup>, the upconverted luminescence from  $^4\text{D}_{3/2}$  level may be interpreted by using the upconversion energy transfer mechanisms depicted in figure 6:



The energy values are from [4].  $17095\text{cm}^{-1}$  is the position of the lowest Stark level of  $^2\text{G}_{7/2} + ^4\text{G}_{5/2}$  multiplets. The above cross - relaxation process ( mismatch is  $4\text{cm}^{-1}$  ) excites resonantly  $\text{Nd}^{3+}$  to

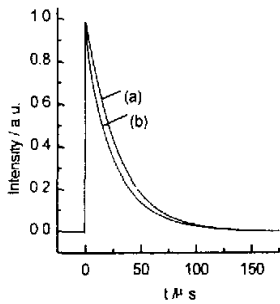


Fig. 5 Luminescence decay after resonant excitation to  ${}^2G_{7/2} + {}^4G_{5/2}$  of  $\text{Nd}^{3+}$ :  $\text{LaCl}_3$  at 12K

- (a) laser set at 578.2nm with a low power.  
 (b) laser set at 582.6nm with a high power where the upconversion - luminescence of Fig.1 occurs.

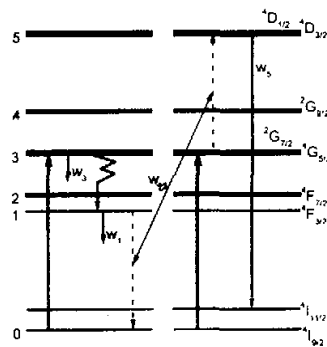


Fig. 6 Model for upconverted - luminescence  
 - - - : transitions induced by the laser,  
 — luminescence transitions, ··· transitions induced by the inner - ionic coupling.

their  ${}^4D_{3/2}$  state and from there, the  ${}^4D_{3/2}$  level is populated via a rapid non - radiative relaxation. The long lifetimes of  ${}^4G_{5/2}$  and  ${}^4F_{3/2}$  levels are in favor of the upconversion process. According to the model depicted in figure 6, the following rate equations can be written:

$$\begin{aligned} \frac{dn_1}{dt} &= -(w_1 + w_{11})n_1 = -\left(\frac{1}{\tau_1} + \frac{1}{\tau_{11}}\right)n_1 = -\frac{n_1}{\tau_1'} \\ \frac{dn_3}{dt} &= -(w_3 + w_{31})n_3 = -\left(\frac{1}{\tau_3} + \frac{1}{\tau_{31}}\right)n_3 = -\frac{n_3}{\tau_3'} \\ \frac{dn_5}{dt} &= -w_5n_5 + w_{31}n_3 = -\frac{n_5}{\tau_5} + \frac{1}{\tau_{31}}n_3 \end{aligned}$$

Where  $n_i$  stands for the population in level  $i$  ( $i=1, 3, 5$ ),  $w_i$  is the relaxation rate and  $w_i = 1/\tau_i$ . The energy transfer process that couples the  $\text{Nd}^{3+}$  is described by the parameter  $w_{31}$ . Using  $n_5(0) = 0$ , the equations can be solved:

$$n_5(t) = \frac{w_{31}N_1(0)N_3(0)}{1/\tau_5 - 1/\tau} (e^{-t/\tau} - e^{-t/\tau_5}) \quad (1)$$

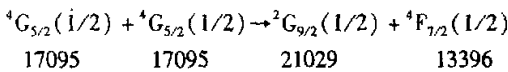
$$1/\tau = 1/\tau_1' + 1/\tau_3'$$

The fit of the upconversion transient of  ${}^4D_{3/2}$  emission with equation (1) gives a rise and a decay time of 4.5 and 24.6 $\mu\text{s}$  respectively. In order to be able to compare with our model, we need to know the values of  $\tau_i$ ,  $i=1, 3, 5$  and  $\tau_{11}$ . This was done as follows: The luminescence lifetimes of  ${}^4D_{3/2}(\tau_5)$  and  ${}^4G_{5/2}(\tau_3)$  levels at 12K were determined by direct selective excitation of these levels (Table 1). Then, by using the decay time values of 29.2 $\mu\text{s}$  ( $\tau_3$ ) and 28 $\mu\text{s}$  ( $\tau_3'$ ) determined from curves (a) and (b) in figure 5 and the lifetime value of  ${}^4F_{3/2}$  level (206 $\mu\text{s}$ ) measured by Partlow and Moos<sup>[12]</sup>,  $\tau_{11}$  was calculated as 681 $\mu\text{s}$ . According to the model, the variation of the intensity of  ${}^4D_{3/2}$  emission should have a rise time,  $\tau_5 = 10.3\mu\text{s}$  and a decay time,  $\tau = 23.8\mu\text{s}$ . The decay time fits well the experimental value of 24.6 $\mu\text{s}$  plotted in figure 4(a) within experimental errors, but the measured value of rise time, 4.5 $\mu\text{s}$ , is smaller than the predicted one. This disagreement implies that the upconversion process discussed above is not the only one that may be involved in the energy

relaxation step. Among other processes, the excited - state absorption from the lowest stark level of <sup>4</sup>G<sub>5/2</sub> at 17095cm<sup>-1</sup> to <sup>2</sup>H'<sub>11/2</sub>(3/2) state at 34265cm<sup>-1</sup> (not shown in the figure) has the greatest probability with an energy mismatch of 6cm<sup>-1</sup>. During this process, <sup>4</sup>D<sub>3/2</sub> level is populated via fast non - radiative relaxations and the new opened channel results in a shorter rise time. Excitation spectra in figure 2 support this explanation. As pointed out before, the main peak at 582.6nm is much sharper in upconversion luminescence than for the Stokes emission. The reason of this narrowing is the above mentioned excited - state absorption process which limits the absorption wavelength range, leading to a sharper excitation peak.

From τ<sub>el</sub>, the upconversion rate constant can be calculated as w<sub>el</sub> = 1/τ<sub>el</sub> = 1468s<sup>-1</sup>. Compared to other materials, especially CsCdBr<sub>3</sub>: Er studied by Cockroft *et al.*<sup>[13]</sup> providing rate constant values between 128 to 1942s<sup>-1</sup>, our rate is at the higher end of this range, indicating that the studied upconversion process is quite efficient in Nd<sup>3+</sup>: LaCl<sub>3</sub>.

The other upconversion luminescence involving <sup>2</sup>G<sub>9/2</sub> level can be well explained by ETU mechanism. Inspection of the Nd<sup>3+</sup> energy levels<sup>[4]</sup> shows that the process (Fig. 7)



can populate <sup>2</sup>G<sub>9/2</sub> level. This process is not resonant (mismatch 235cm<sup>-1</sup>), but it may easily be fulfilled by the lattice vibrations. According to the model, one can write the following kinetics equations

$$\begin{aligned}
 \frac{dn_4}{dt} &= -w_4 n_4 + w_2 n_3 n_3 = -\frac{n_4}{\tau_4} + \frac{n_3 n_3}{\tau_2} \\
 n_4(t) &= \frac{w_2 N_3^2(0)}{2/\tau_3' - 1/\tau_4} (e^{-t/\tau_4} - e^{-2t/\tau_3'}) \quad (2)
 \end{aligned}$$

Differently from the above discussion for <sup>4</sup>D<sub>3/2</sub> level, we used n<sub>3</sub> = N<sub>3</sub>(0)e<sup>-t/τ<sub>3</sub>'</sup> to simplify the problem. This is an acceptable approximation because the upconversion luminescence involving <sup>2</sup>G<sub>9/2</sub> level is much weaker than that originating in <sup>4</sup>D<sub>3/2</sub> (Fig. 1). In this case, the lowest order of rate equations can be used. Equation (2) tells us that the transient of <sup>2</sup>G<sub>9/2</sub> emission has a rise time τ<sub>rise</sub> = (1/2)τ<sub>3</sub>' = 14μs and a decay time τ<sub>d</sub> = 87.6μs. These values are consistent with the values 12.9 and 89.6μs determined from experiment, indicating that our model describes the process correctly.

### 5 Conclusion

We have shown that blue and near violet upconversion luminescence from Nd<sup>3+</sup>: LaCl<sub>3</sub> at low temperature can be obtained under excitation with yellow laser frequency. Depending upon the emission level, the mechanism is energy transfer with or without excited - state absorption. The upconversion rate constant at 12K for <sup>4</sup>D<sub>3/2</sub> → <sup>4</sup>I<sub>11/2</sub> transition is determined as w<sub>el</sub> = 1468s<sup>-1</sup>. Lifetimes of the

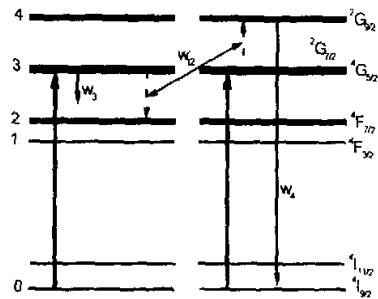


Fig. 7 Model for upconverted - luminescence

- transitions induced by the laser,
- - - luminescence transitions,
- ⋯ transitions induced by the inner
- ionic coupling.

main luminescent levels of  $\text{Nd}^{3+}$  in  $\text{LaCl}_3$  and  $\text{NdCl}_3$  were also determined. The values for  ${}^2\text{G}_{9/2}$  and  ${}^4\text{G}_{7/2}$  levels in  $\text{Nd}^{3+} : \text{LaCl}_3$  are found to be larger than those already reported and the results for  $\text{NdCl}_3$ , to our best knowledge, are new.

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## $\text{Nd}^{3+} : \text{LaCl}_3$ 中的上转换发光研究\*

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**摘要:** 当用 582.6 nm 的黄色激光激发  $\text{Nd}^{3+} : \text{LaCl}_3$  的  ${}^2\text{G}_{7/2} + {}^4\text{G}_{5/2}$  能级时, 观察到了  ${}^4\text{D}_{3/2}$  和  ${}^2\text{G}_{9/2}$  能级的兰光和紫外发射。研究表明,  ${}^2\text{D}_{3/2}$  上转换的机理是能量传递和激发态吸收, 而  ${}^2\text{G}_{9/2}$  则是由于  ${}^4\text{G}_{5/2} + {}^4\text{G}_{5/2} \rightarrow {}^2\text{G}_{9/2} + {}^4\text{F}_{7/2}$  交叉驰豫过程。通过对 12K 下  ${}^4\text{D}_{3/2} \rightarrow {}^4\text{I}_{11/2}$  荧光衰减曲线的分析, 得出能量传递几率为  $w_{11} = 1468 \text{ s}^{-1}$ 。测量和讨论了  $\text{Nd}^{3+} : \text{LaCl}_3$  和  $\text{NdCl}_3$  主要发光能级室温和 12K 下的寿命。

**关键词:** 能量上转换; 传递几率; 寿命;  $\text{Nd}^{3+} : \text{LaCl}_3$  和  $\text{NdCl}_3$  晶体

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