

Colour chart

Establishing the causes of colouring in iron oxide pigments

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Synthetic iron oxides are an important group of inorganic colour pigments, with annual consumption around one million metric tonnes. But even though these products have been used extensively their colouring mechanism (causes of colouring) has not been described sufficiently to date. Detailed descriptions of colouring for red, yellow, orange and black iron oxides is provided and explained, using structural features of each and findings from ligand field and molecular orbital (MO) theory.

Iron oxide red pigments

Colouring inorganic pigments is commonly produced by a combination of light absorption and diffusion in the visible spectral range. The tests performed were carried out on phase-pure iron oxide pigments that are grouped together with selected properties in *Table 1*. α -Fe₂O₃ pigments have the crystal structure of the corundum and contain only octahedrally coordinated Fe(III) ions in a high-spin state, i.e. all five 3d electrons are unpaired, which is particularly important for the electron structure and thus the colouring.

The products exhibit a virtually isometric habit (spherical to cube-shaped). Average particle diameter varied in a range from around 0.08 to 1.0 µm.

The smallest unit in oxidic iron(III) materials is formed by regular Fe(III)O₆ octahedra, each with six identical Fe-O distances of around 2.05 Å.

Fe₂O₃ double octahedra with common faces are present in the hematite lattice, with the Fe(III) ions occupying only 2/3 of the available octahedron positions, while the oxygen lattice section is full. As a result of the unoccupied

Fe(III) positions, a deficit in positive charge is produced that is compensated by moving the Fe(III) ions from the centre of the octahedra. This leads to pronounced distortion for the two individual octahedra (trigonal components). As a result, the Fe-O distances vary greatly (3 x 2.12 Å and 3 x 1.95 Å in the respective individual octahedron) and the Fe(III)-O-Fe(III) angle is approximately 85°.

Light absorption and colouring

When considering a hematite single crystal and a powder α -Fe₂O₃ pigment, in both cases the green and blue spectral ranges of the incident light are absorbed selectively. The unabsorbed proportion of visible light (600 – 720 nm) causes the red colour impression.

To investigate selective light absorption without influence from light diffusion, the absorption spectrum of a hematite single crystal was first recorded at room temperature (RT) and is shown in *Figure 1*. [2]

The x axis shows the wave number (in cm⁻¹) and wavelength (in nm) and provides the energy positions of the absorption bands.

The y axis shows extinction E and enables quantitative data relating to the intensities of the absorption bands. (The scale is logarithmic, i.e. there is a difference of 10⁴ between E = 0 and E = 4.)

The correlation

$$E = \log I_0/I = \epsilon \cdot d$$

applies to absorbance, with I₀ indicating the intensity of the incident light and I the intensity of the transmitted light.

ε describes a solid's absorption properties and d expresses the single crystal's layer thickness.

Bands I (11,600 cm⁻¹ (approximately 860 nm), intensity of approximately 10) and II (15,700 cm⁻¹ (approximately 635 nm) as a shoulder with an intensity of approximately 12) of the absorption spectrum are due to the two initial electron transitions of the d⁵ electron system of the iron(III) ions in octahedral oxygen coordination.[3]

The sharp and intense rise in absorption with a wide plateau extending up to the UV range (from 16,800 cm⁻¹ (approximately 595 nm) with an intensity of around 10,000) is caused by a large number of other electron transitions of the d⁵ multiple electron system. [3]

The very high intensities are caused by the particular spin-spin interactions of the unpaired 3d electrons of two iron(III) ions in the double octahedra by way of the bridging oxygen anions (Fe-O-Fe angle approximately 85°). [4]

The intensity of this absorption range is increased further by the rise to the first electron transfer band (transfer of an electron from the O²⁻ ligand to the iron(III) central atom), which is widest in the range from approximately 30,000 cm⁻¹ to 35,000 cm⁻¹ and also exhibits very high intensity. The precise band position can be calculated using MO theory. [5]

Table 1: Tested iron oxide pigments with selected properties

Pigment type*	Chemical composition and oxidation level of the iron	Lattice type	Structural features
Iron oxide red (hematite)	α -Fe ₂ O ₃ (Fe(III) ions)	Corundum (α -Al ₂ O ₃)	Fe ₂ O ₃ double octahedra with common faces
Iron oxide yellow (goethite)	α -FeOOH (Fe(III) ions)	Diaspore (α -AlOOH)	Edge-sharing FeO ₃ (OH) ₃ octahedra
Iron oxide orange (lepidocrocite)	γ -FeOOH (Fe(III) ions)	Boehmite (γ -AlOOH)	Edge-sharing FeO ₃ (OH) ₃ octahedra
Iron oxide black (magnetite)	Fe ₃ O ₄ (Fe(II) and Fe(III) ions)	Inverse spinel	Fe(II)/Fe(III) octahedra Fe(III) tetrahedrons

* Phase purity was determined using the XRD method

A quantitative evaluation of all electron transitions of $\text{Fe(III)}\text{O}_6$ octahedra is possible using ligand field theory and provides the electron structure of $\alpha\text{-Fe}_2\text{O}_3$ in the d^5 multiple electron system. *Figure 6* shows the simplified term structure with the measured (I and II) and calculated (III to VI) electron transitions in the visible spectral range. [6]

Unlike single crystals, both absorption and scattering properties need to be taken into account to explain colouring for powder iron oxide red pigments. When measuring pigment powders, the part of the light that provides colour (red spectral range) is first scattered several times on the pigment particles and then enters the spectrometer (integrating sphere) as diffused light.

To obtain the absorption spectrum from the remission spectrum thus measured, the measured remission values $R(\nu, \lambda)$ need to be converted using the Kubelka-Munk equation

$$\frac{K}{S} = \frac{(1-R_\infty)^2}{2R_\infty}$$

and plotted against the wave number / wavelength as K/S .

Results at a glance

» Colouring inorganic pigments is commonly produced by a combination of light absorption and diffusion in the visible spectral range. Tests performed were carried out on phase-pure iron oxide red, yellow, orange and black pigments using structural features of each and findings from ligand field and molecular orbital (MO) theory.

» For iron oxide red pigments rises in absorption become much less intense as particle size increases, and the steepness is reduced. A slight shift toward lower wave numbers also occurs. These changes result in a distinct bluish cast and a dirtier colour impression compared to the red pigments I, II and III.

» For iron oxide yellow pigments, as a result of these different ligand field parameters, the high-intensity absorption bands III to VI for $\alpha\text{-FeOOH}$ are positioned much more in the short-wave range, with the result that the rise in absorption that determines colour also undergoes a significant UV shift.

» For iron oxide orange pigments, the calculation of electron transitions I to IV provides a very good correlation with the measured band positions I to IV, as shown in *Figure 7*, and thus explains the colour change from yellow to orange.

» For iron oxide black pigments, at RT, the octahedrally coordinated iron ions have an average valence of + 2.5, which Mössbauer spectroscopy also demonstrates with a signal split as a sextet, as the "Fe^{2.5+} ions" couple magnetically with the tetrahedrally coordinated iron(III) ions.

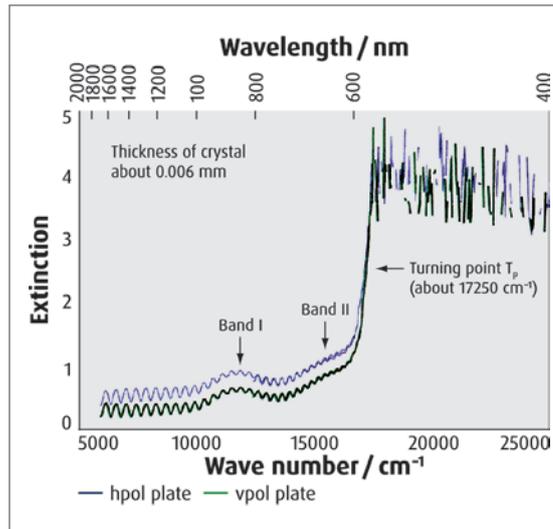


Figure 1: Single crystal absorption spectrum of $\alpha\text{-Fe}_2\text{O}_3$

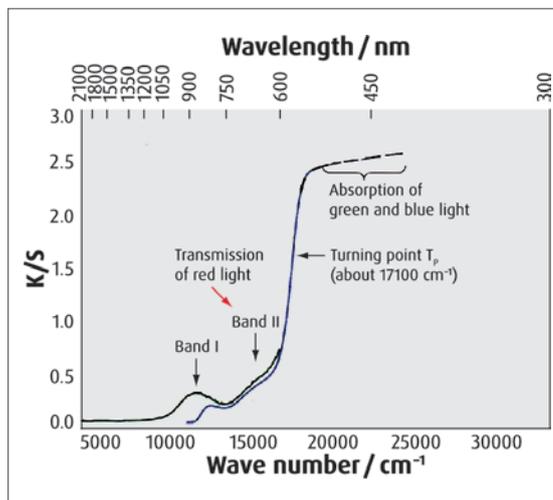


Figure 2: Absorption spectrum of iron oxide red III

K is the absorption coefficient of the red pigment and correlates with the extinction (absorbance) E of the single crystal through the relationships

$$K = 2.302 \cdot \epsilon \cdot d \text{ and } E = \epsilon \cdot d.$$

With the exception of the factor 2.302, single crystal and pigment powder have comparable dependencies in terms of absorption properties.

S is a pigment's scattering coefficient and is essentially dependent on particle size and the refractive index n .

Figure 2 shows the absorption spectrum of a red pigment with an average particle size of approximately $0.25 \mu\text{m}$ (red III). Bands I and II have virtually the same energy positions as for measurement of the single crystal, as shown in *Figure 1*. This is logical given the identical electron structure of the $\alpha\text{-Fe}_2\text{O}_3$ materials. The correct magnitude of intensities is only obtained by measurement of the $\alpha\text{-Fe}_2\text{O}_3$ single crystal. The absorption spectrum of a saturated cadmium red pigment ($\text{CdS}_x\text{Se}_{1-x}$ mixed phase), as shown in *Figure 3*, features a very steep, sudden rise in absorption that is caused by direct electron transitions from the valence

band (VB) to the conduction band (CB). In the case of α - Fe_2O_3 pigments, the rise in absorption is less steep (angle of inclination α at the turning point T_p is approx. 80° compared to 85° for the cadmium red pigment) and the

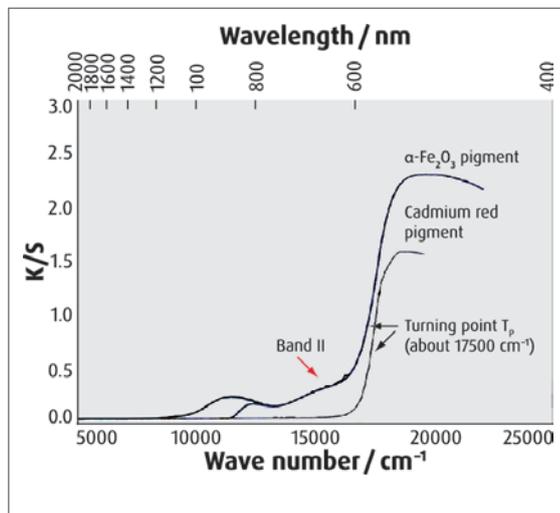


Figure 3: Absorption spectrum of α - Fe_2O_3 and comparison with a cadmium red pigment

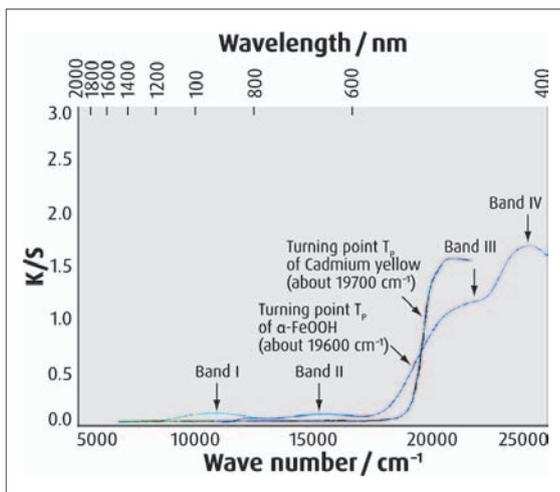


Figure 4: Absorption spectrum of α - FeOOH and comparison with a cadmium yellow pigment

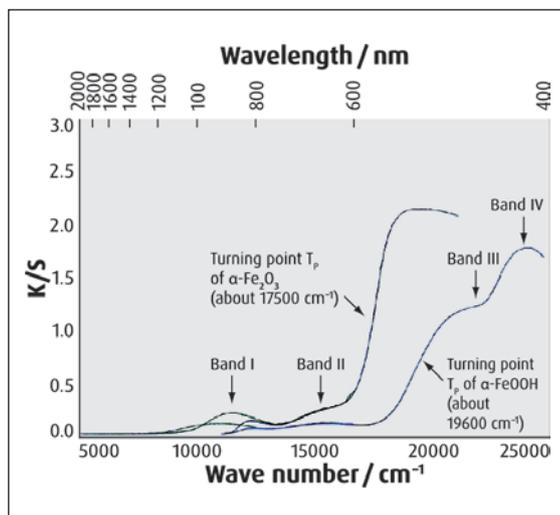


Figure 5: Absorption spectra of α - FeOOH and comparison with α - Fe_2O_3 pigment

steepness is also reduced by band II at approx. $15,500\text{ cm}^{-1}$.

These differences lead to the α - Fe_2O_3 pigments being much less saturated and exhibiting much lower colour purity.

The influence of particle size on pigment colouring properties is well known. To also investigate this spectroscopically, red pigments of various particle sizes from magnetite precursors were produced using the Laux process (characterisation in line with Table 2.) and investigated spectroscopically.

If considering the red pigments I to V, red III represents the reference point (average particle size approximately $0.25\text{ }\mu\text{m}$). With increasing fineness, the colour shifts toward more yellowish products (red I and red II). When the pigment particles are increased, a significant blue shift occurs (red IV and red V).

In the transition from red III to red pigments II and I (increasing fineness), the profile of the absorption spectra is very similar (same positions for bands I and II). However, a difference exists for the intensities of band II, as decreasing particle size is accompanied by a reduction, shown in Table 2, which results in the somewhat greater colour saturation for the finer pigments. If we consider the rises in absorption, it is possible to observe a shift toward the short wave from red III to red II and red I (see inflection points in Table 2), which explains the yellow tinge of the finer red. The intensities for the finer pigments are also slightly lower than for red III.

In the transition from red III to the red pigments IV and V (increasing particle size), the energy positions of bands I and II in the absorption spectra are also comparable to red III, while the intensities of band II are slightly higher, which Table 2 shows.

The rises in absorption become much less intense as particle size increases, and the steepness is reduced. A slight shift toward lower wave numbers also occurs. These changes result in a distinct bluish cast and a dirtier colour impression compared to the red pigments I, II and III.

Iron oxide yellow pigments

Iron oxide yellow (goethite, α - FeOOH) has the crystal structure of diasporite (α - AlOOH) and contains only Fe(III) ions in an octahedral coordination. The pigments exhibit a needle-shaped habit, with a length-to-width ratio of around 5 : 1 predominating.

The smallest structural units for α - FeOOH are $\text{FeO}_3(\text{OH})_3$ octahedra, where the iron(III)-ion is coordinated asymmetrically by three oxygen (O^{2-}) and three hydroxyl (OH^-) ligands.

This distortion of the individual octahedra becomes clear if we look at the Fe-O and Fe-OH distances:

Fe-O with $1 \times 1.89\text{ \AA}$ and $2 \times 2.02\text{ \AA}$

Fe-OH with $1 \times 2.05\text{ \AA}$ and $2 \times 2.12\text{ \AA}$

In the crystal lattice of the goethite, these $\text{FeO}_3(\text{OH})_3$ individual octahedra form double chains through shared edges and these chains are linked to each other via corners, thus creating tunnel-like cavities [1].

There are also hydrogen bonds between the double chains, with the hydrogen atoms being located essentially in the "tunnels" of the crystal.

Absorption spectrum and colouring

At 21,500 cm^{-1} (band III) and 24,000 cm^{-1} (band IV), the absorption spectrum of a yellow pigment, shown in *Figure 7*, exhibits two intensive absorption maximums that determine colouring.

The high intensity of the two bands is due to electron transitions with particular spin-spin interactions of the five unpaired 3d electrons of two adjacent Fe(III) ions in the crystal lattice, with the rise in absorption adding additional intensity to the first electron transfer band from the $\text{O}^{2-}/\text{OH}^-$ to the Fe(III) cation. A disadvantage for the saturation and colour purity of the α -FeOOH pigments is the relatively flat rise in the range from 18,500 to 20,500 cm^{-1} (angle of inclination α at the turning point T_p of approx. 64°). In contrast, the rise in absorption of the brilliant cadmium yellow pigment is much steeper (angle α approx. 84° , as shown in *Figure 4*)

The two wide and low-intensity bands at 10,850 cm^{-1} (I) and 15,500 cm^{-1} (II) have no significant impact on colouring of α -FeOOH pigments.

Although the electron structures of red and yellow are very similar, a distinct short-wave shift in the rise in absorption of around 2,100 cm^{-1} can be detected when comparing the absorption spectra, which is shown in *Figure 5*. An explanation for this is provided by ligand field theory in conjunction with the structural differences of the two pigments.

Fe_2O_3 double octahedra with common faces are present in the α - Fe_2O_3 , while edge-sharing $\text{FeO}_3(\text{OH})_3$ individual octahedra can be observed in the α -FeOOH.

In accordance with ligand field theory, the OH^- ion is a stronger ligand than the O^{2-} ion [3,5], with the result that a much higher ligand field strength Δ is calculated for α -FeOOH than for α - Fe_2O_3 following evaluation of the two absorption spectra ($\Delta\alpha$ -FeOOH = 13,600 cm^{-1} and $\Delta\alpha$ - Fe_2O_3 = 11,300 cm^{-1}). The covalence parameter B was fixed at 580 cm^{-1} (α - Fe_2O_3) and 630 cm^{-1} (α -FeOOH), i.e. the Fe-O bonds in the α - Fe_2O_3 exhibit higher covalence components.

As a result of these different ligand field parameters, the high-intensity absorption bands III to VI for α -FeOOH are positioned much more in the short-wave range [6], with the result that the rise in absorption that determines colour also undergoes a significant UV shift.

Iron oxide orange pigment

Lepidocrocite (γ -FeOOH) has a boehmite structure (γ -AlOOH). The smallest structural units are $\text{FeO}_3(\text{OH})_3$ octahedra that have three different Fe-O distances with 2 x 1.93 Å, 2 x 2.05 Å and 2 x 2.13 Å.

In the crystal lattice of the lepidocrocite, these individual octahedra form double chains through shared edges, these chains developing slightly waved layers at the b/c level of the elementary cell with further double chains. [1] The individual layers are finally bonded by means of hydrogen bonds, similar to α -FeOOH.

Light absorption and colouring

The absorption spectrum of γ -FeOOH is very similar to that of α -FeOOH, which is shown in *Figure 6*.



WHAT'S YOUR FAVORITE COLOUR?

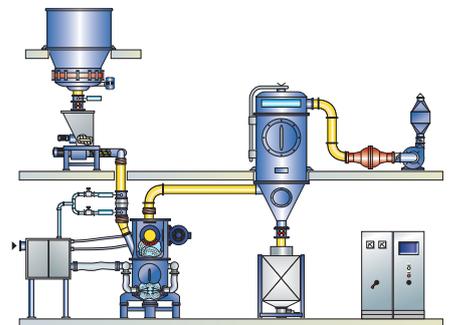
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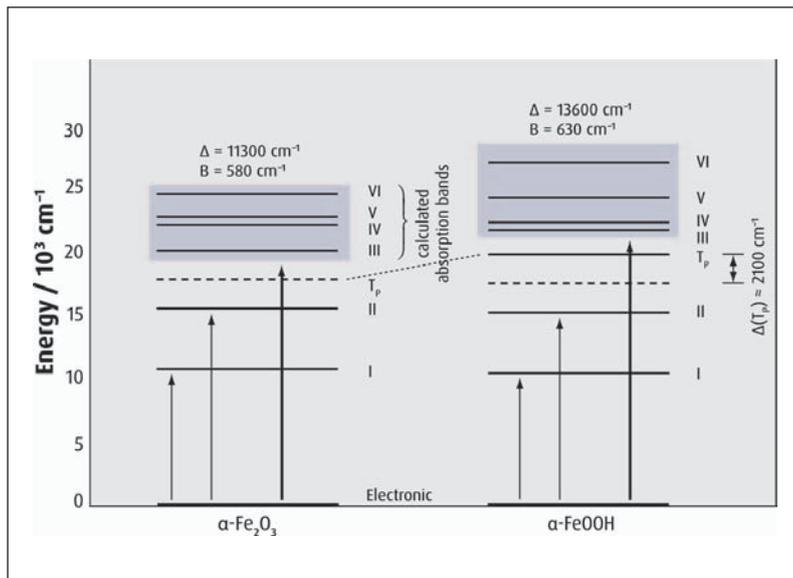


Figure 6: Simplified electron structures of hematite and goethite

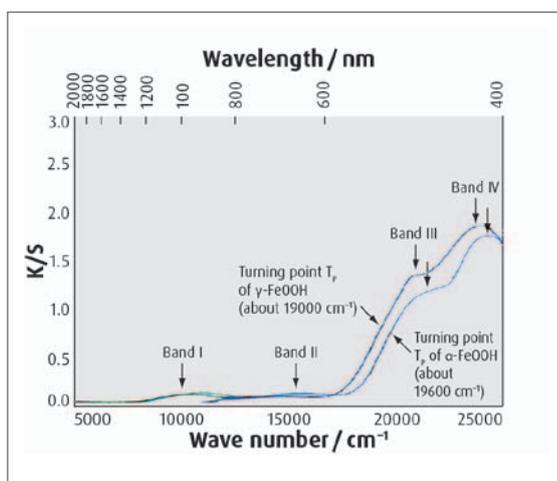


Figure 7: Absorption spectra of α -FeOOH and γ -FeOOH compared

Table 2: Properties of α -Fe₂O₃ pigments with different particle sizes

Product name	Average particle size (µm)	Intensity i Band II	Inflection points I _p Rise in absorption (cm ⁻¹)	Intensity Rise in absorption	b*	(L64, pure tone)
Red I (yellowish cast)	Approx. 0.08	0.20	17,600	2.05	24.1	Yellow shift
Red II (yellowish cast)	Approx. 0.15	0.30	17,300	2.25	23.7	
Red III	Approx. 0.25	0.42	17,100	2.40	20.5	
Red IV (bluish cast)	Approx. 0.70	0.50	16,700		8.3	
Red V (strongly bluish cast)	Approx. 1.0	0.50	Approx. 16,500	0.70	5.5	

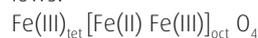
The rise in absorption for band III exhibits a steepness that is comparable with that of band III for α -FeOOH, but the position of this rise for γ -FeOOH has been shifted around 600 cm⁻¹ in the long-wave direction, shown in Figure 7, which causes the colour shift to orange.

This longer-wave position of bands III and IV for γ -FeOOH can be explained using ligand field theory if the differences in the hydrogen bonds are also taken into account. In the case of γ -FeOOH, these hydrogen bonds are less pronounced due to the differing linking of the octahedron chains, so that a somewhat stronger ligand field results for the Fe(III) ions, which leads to a higher Δ value (14,000 cm⁻¹ as opposed to 13,600 cm⁻¹ for α -FeOOH). The covalence of the Fe-O bonds is comparable to the two pigments due to the calculated B values of 630 cm⁻¹.

On this basis, the calculation of electron transitions I to IV provides a very good correlation with the measured band positions I to IV, as shown in Figure 7, and thus explains the colour change from yellow to orange. [6]

Causes of colouring in iron oxide black pigments

The chemical composition and distribution of Fe(II) and Fe(III) ions in the spinel lattice can be described as follows:



Ideally, the ratio of Fe(II) and Fe(III) ions to octahedron positions is 1 : 1, with the respective octahedra being linked via shared edges. At RT, the two octahedron positions cannot be distinguished, with the result that a fast electron transition from Fe(II) to Fe(III) can occur that requires only minimal excitation energies. This energy is $\geq 1,000$ cm⁻¹, i.e. the entire visible light and part of the infrared light are absorbed virtually completely, thus forming the black colour of the magnetite.

At RT, the octahedrally coordinated iron ions have an average valence of + 2.5, which Mössbauer spectroscopy also demonstrates with a signal split as a sextet, as the "Fe^{2.5+} ions" couple magnetically with the tetrahedrally coordinated iron(III) ions. Further evidence for the indistinguishability of iron ions in octahedron positions is provided by neutron diffraction with an Fe-O distance of only 2.06 Å. [7]

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