

**BMM 205**

# Malzeme Biliminin Temelleri

## Katıların Kristal Yapıları

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**Malzeme Bilimi ve Nanoteknoloji Mühendisliği Bölümü**

**TOBB Ekonomi ve Teknoloji Üniversitesi**

**Ankara - TÜRKİYE**

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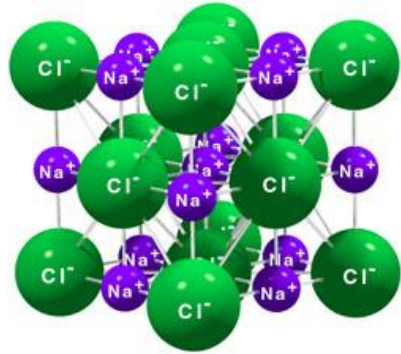
<http://eeoren.etu.edu.tr>



**BİYONANOTASARIM  
LABORATUVARI**

# KATILARIN KRİSTAL YAPILARI

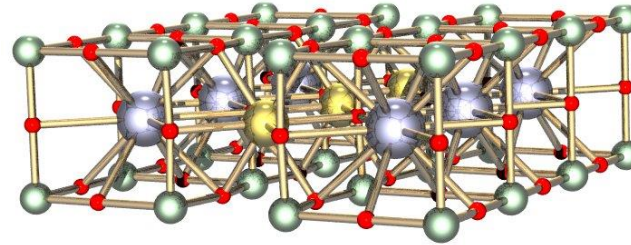
**Kristalografi (Crystallography)** atomların katılar içerisinde nasıl dizildiklerini inceleyen bilim dalıdır. Yunanca *crystallon* (donmuş damla) ve *grapho* (yazmak) kelimelerinden oluşmuştur.



Crystal structure of NaCl

## 1987 Nobel Prize in Physics

J. Georg Bednorz and K. Alexander Müller *for their important break-through in the discovery of superconductivity in ceramic materials.*

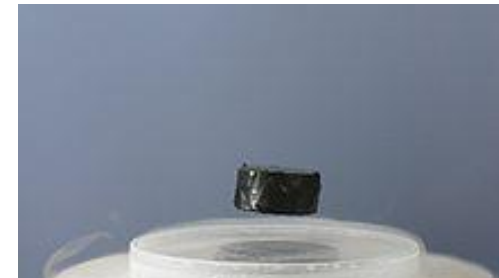
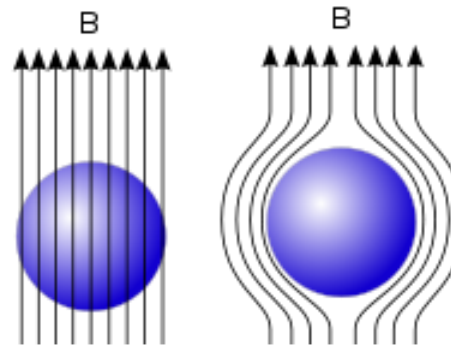
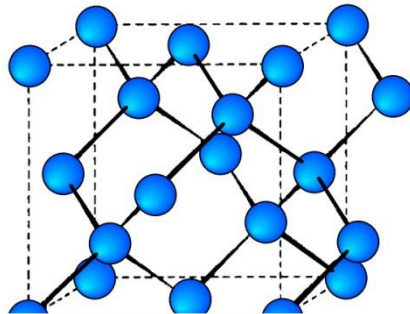


$\text{YBa}_2\text{Cu}_3\text{O}_7$   $T_c = 90 \text{ K}$



Heike Kamerlingh Onnes

1913 Nobel Prize in Physics



# KATILARIN KRİSTAL YAPILARI

**Kristalografi (Crystallography)** atomların katılar içerisinde nasıl dizildiklerini inceleyen bilim dalıdır. Yunanca *crystallon* (donmuş damla) ve *grapho* (yazmak) kelimelerinden oluşmuştur.

Transition temperature (in kelvin)	Transition temperature (in celsius)	Material	Class
195	-78	Sublimation point of Dry Ice	
133	-140	HgBa <sub>2</sub> Ca <sub>2</sub> Cu <sub>3</sub> O <sub>x</sub>	Copper-oxide superconductors
110	-163	Bi <sub>2</sub> Sr <sub>2</sub> Ca <sub>2</sub> Cu <sub>3</sub> O <sub>10</sub> (BSCCO)	
90	-183	YBa <sub>2</sub> Cu <sub>3</sub> O <sub>7</sub> (YBCO)	
77	-196	Boiling point of liquid nitrogen	
55	-218	SmFeAs(O,F)	Iron-based superconductors
41	-232	CeFeAs(O,F)	
26	-247	LaFeAs(O,F)	
20	-253	Boiling point of liquid hydrogen	
18	-255	Nb <sub>3</sub> Sn	Metallic low-temperature superconductors
10	-263	NbTi	
9.2	-263.8	Nb	
4.2	-268.8	Boiling point of liquid helium	
4.2	-268.8	Hg (mercury)	Metallic low-temperature superconductors

Hydrogen sulfide  
Chemical Compound



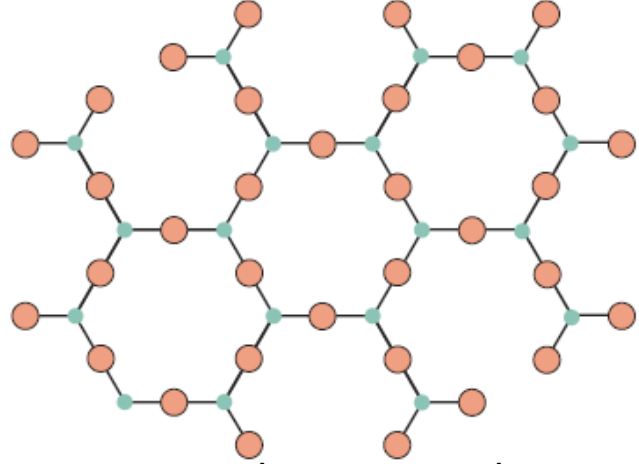
Max Planck Institute for Chemistry, Mainz, Almanya.

$$T_c = 203 \text{ K } (-70 \text{ }^\circ\text{C}) \quad P = 150 \text{ GPa (1.5 milyon atm)}$$

## Katılarda Atom Dizilimleri:

### Kristal

Uzun mesafeli düzenlilik

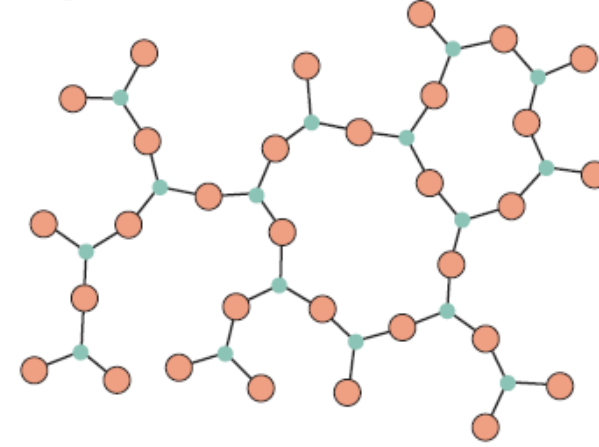


Atomlar sistematik bir şekilde dizilirler



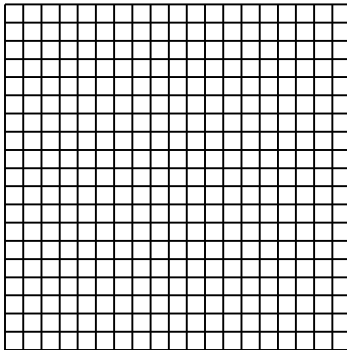
### Amorf (without morphe)

Uzun mesafeli düzenlilik yok

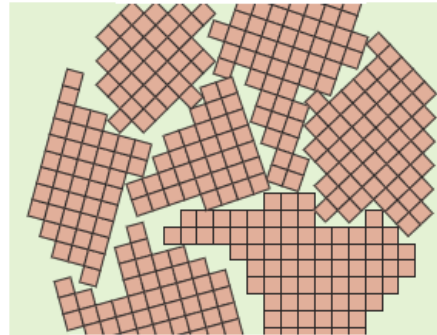


Atom dizilimlerinde herhangi bir sistematik yoktur

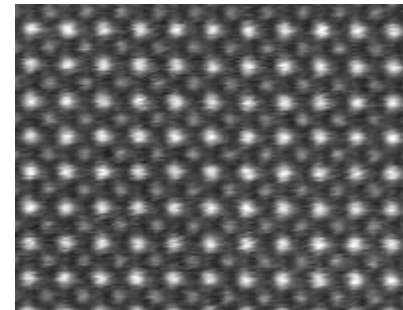
### Tek Kristal



### Poli-kristal

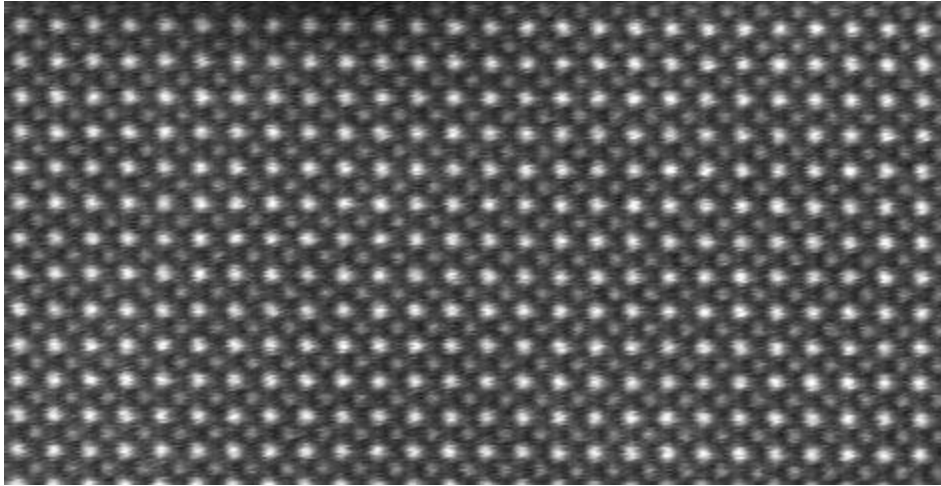


### $\text{SrTiO}_3$



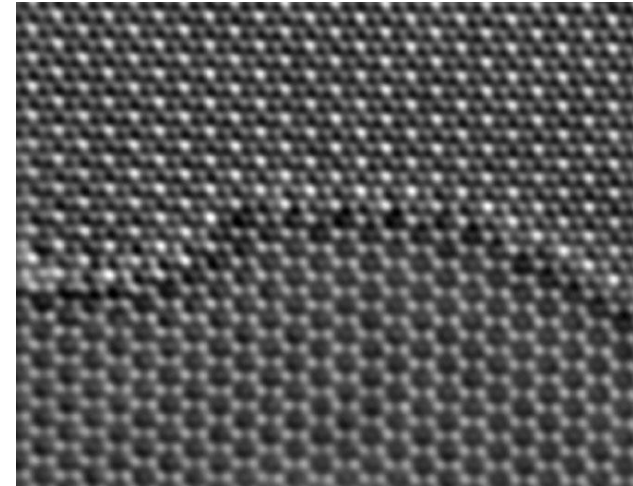
<http://en.wikipedia.org/wiki/Crystallography>

## SrTiO<sub>3</sub>



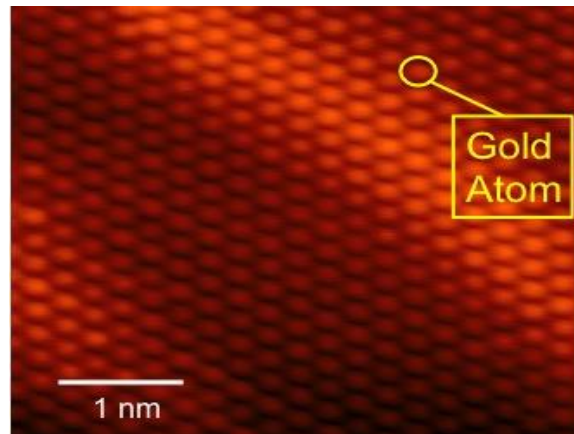
<http://en.wikipedia.org/wiki/Crystallography>

## Graphen



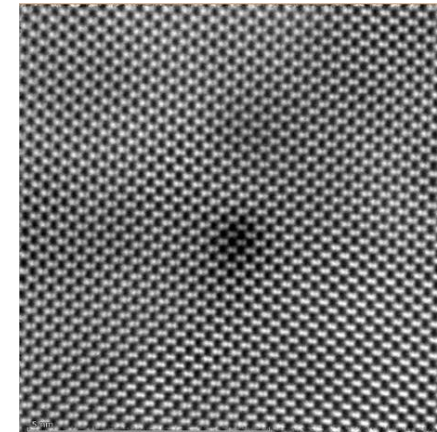
<http://www.nature.com/>

## Altın



<http://www.phys.vt.edu/showcase/index-CME.shtml>

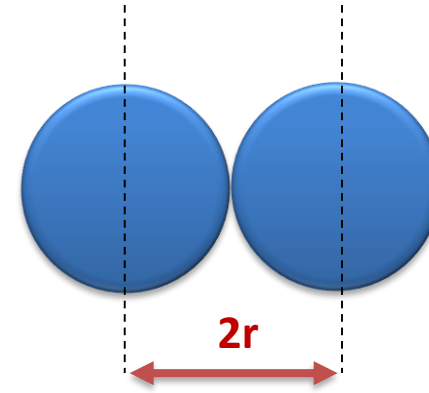
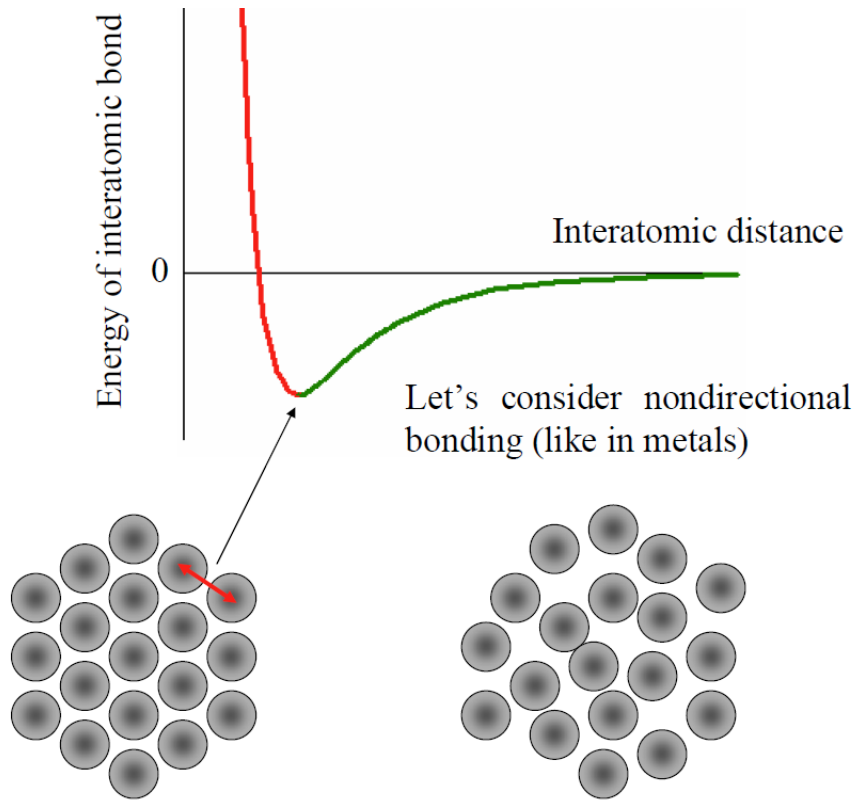
## GaN



<http://www.fei.com/>

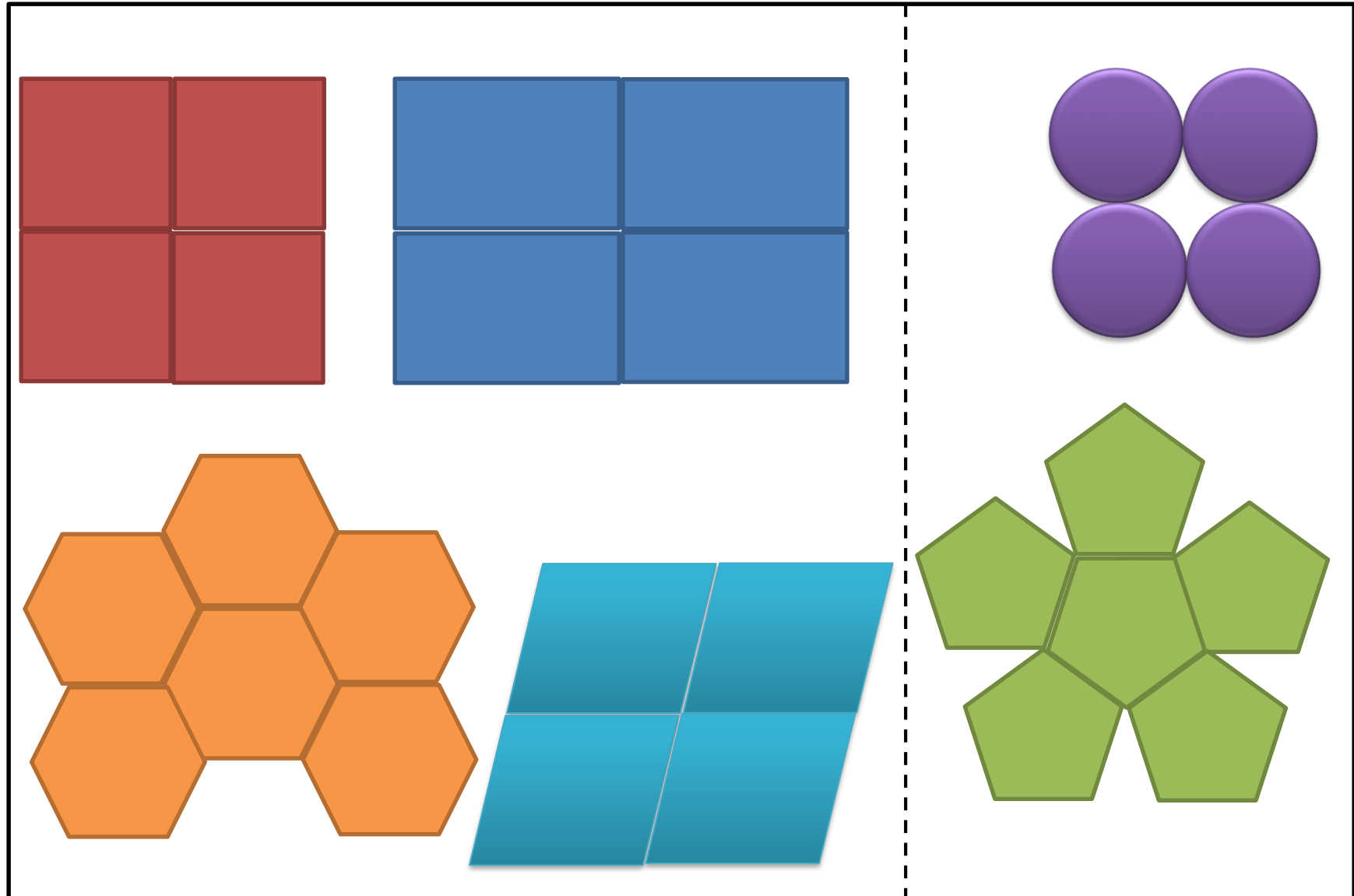
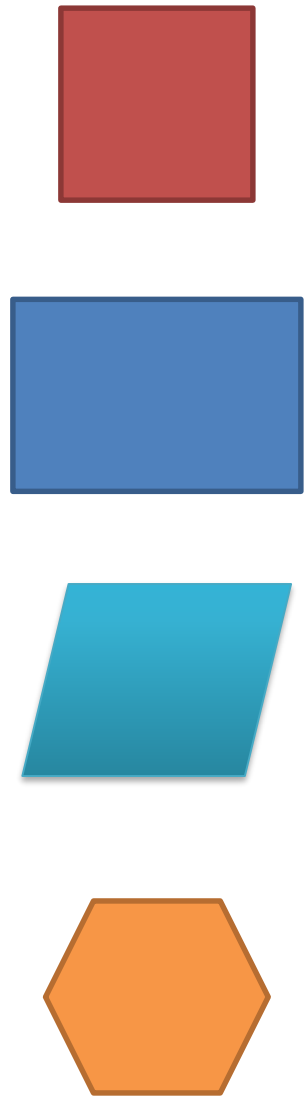
## Kristal Yapılar

Atomlar neden sistematik bir şekilde dizilirler?



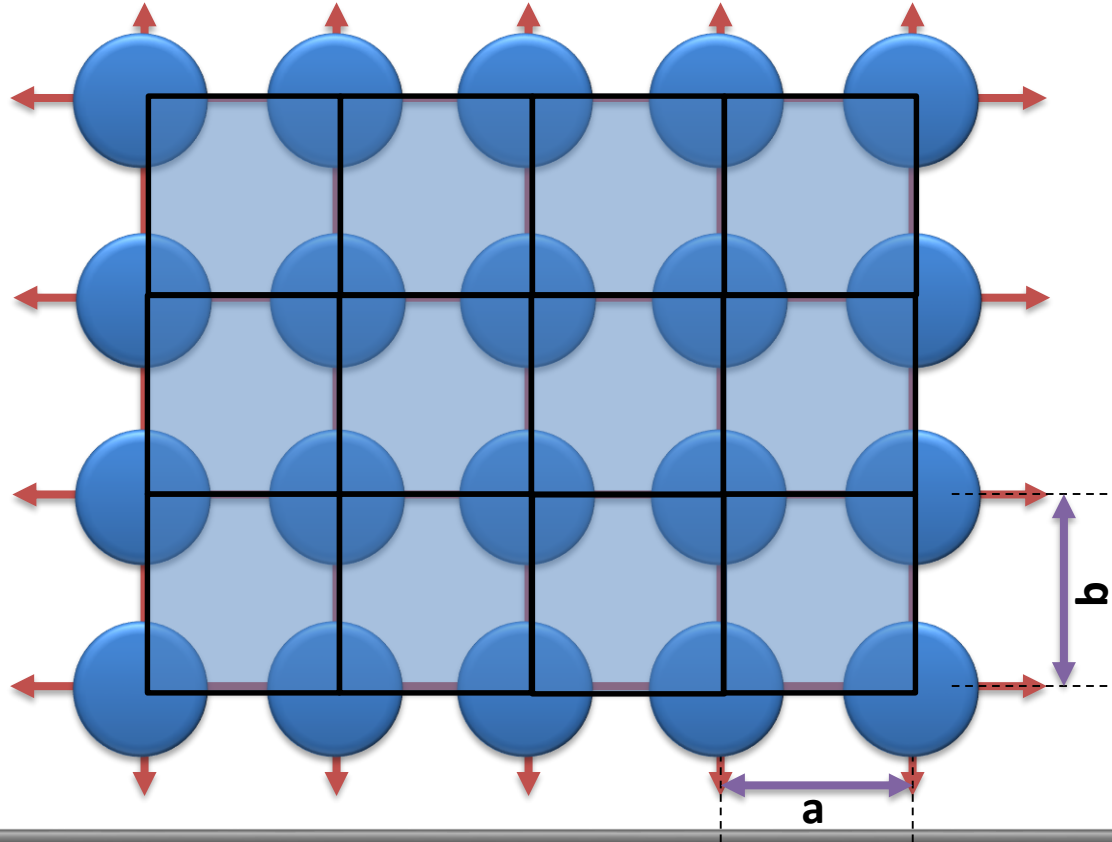
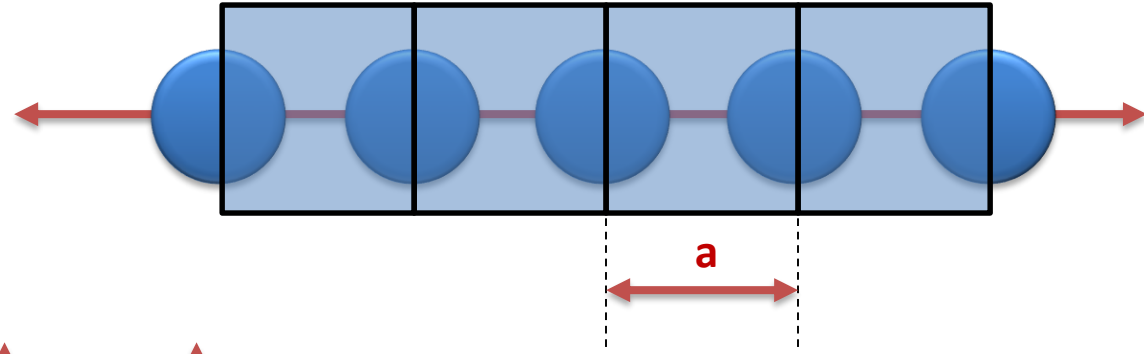
**Sert küre modeli**

# KATILARIN KRİSTAL YAPILARI

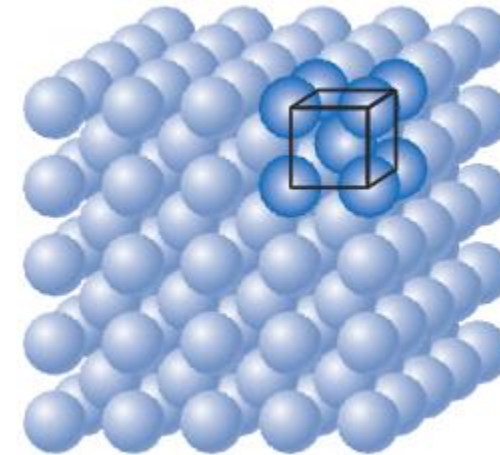


**Atom dizilimleri:** Atomları kaç farklı şekilde dizebiliriz.

1 Boyut	1
2 Boyut	5
3 Boyut	14

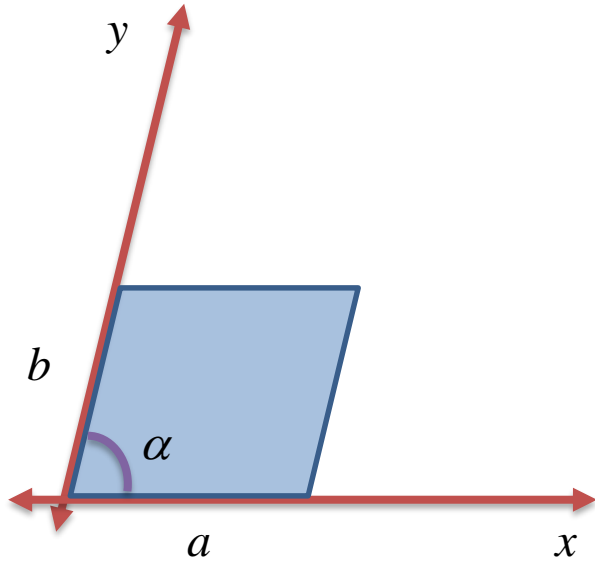


**Birim hücre (Unit cell):** Birim hücre bir kristalin yapısını tarif eden yapısal bir birim veya yapı taşıdır. Birim hücre tekrar edilerek tüm kristal üretilebilir.





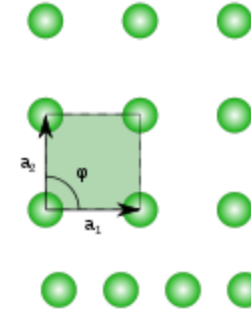
## Birim hücre (Unit cell) 2 Boyut:



**Kafes (lattice) parametreleri:**  
 $a, b, \alpha$ .

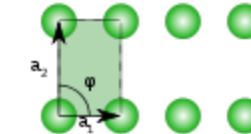
**Kare (square):**

$$a=b, \alpha=90$$



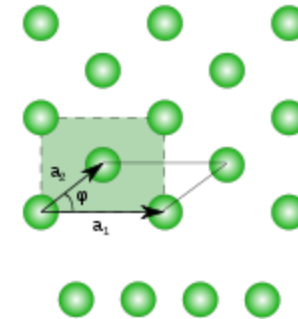
**Dikdörtgen (rectengular):**

$$a \neq b, \alpha=90$$



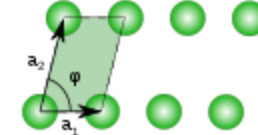
**Merkezli Dikdörtgen (rhombic):**

$$a \neq b, \alpha \neq 90$$



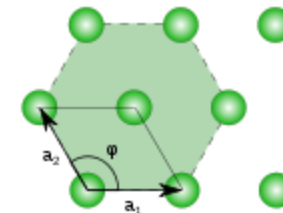
**Oblik (oblique):**

$$a \neq b, \alpha \neq 90$$

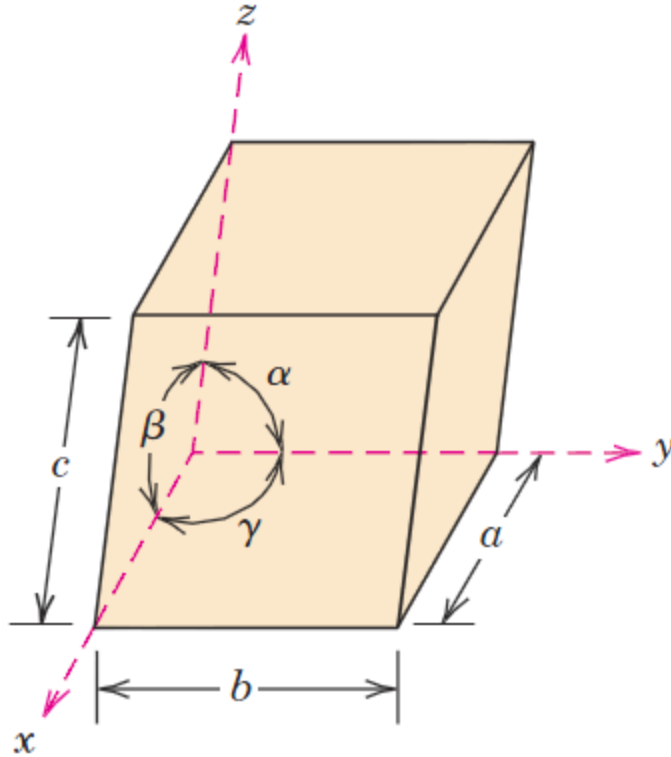


**Altıgen (hexagonal):**

$$a=b, \alpha=120$$

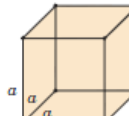
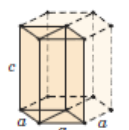
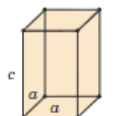
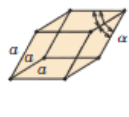
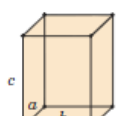
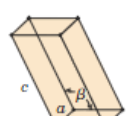
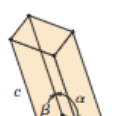


## Birim hücre (Unit cell) 3 Boyut:



**Kafes (lattice) parametreleri:**  
 $a, b, c, \alpha, \beta, \gamma$ .

## Kristal Kafes Sistemleri

Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	
Rhombohedral (Trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta$	
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	

## Bravais Kafes Sistemleri

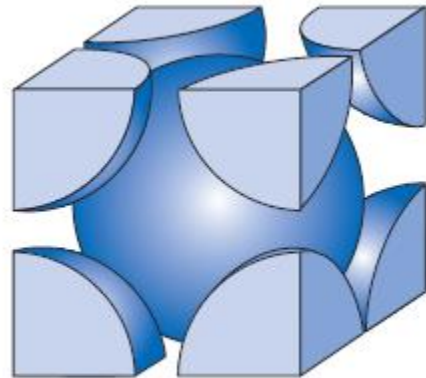
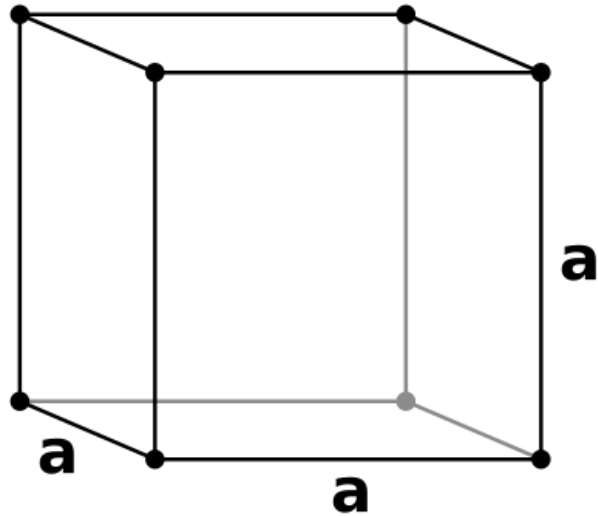
triclinic	P				rhombohedral	P				
	$\alpha, \beta, \gamma \neq 90^\circ$					$\alpha = \beta = \gamma \neq 90^\circ$				
monoclinic	P	C				hexagonal	P			
	$\alpha \neq 90^\circ$ $\beta, \gamma = 90^\circ$	$\alpha \neq 90^\circ$ $\beta, \gamma = 90^\circ$								
orthorhombic	P	C	I	F	cubic	P (pcc)	I (bcc)	F (fcc)		
	$a \neq b \neq c$	$a \neq b \neq c$	$a \neq b \neq c$	$a \neq b \neq c$						
tetragonal	P	I								
	$a \neq c$	$a \neq c$								



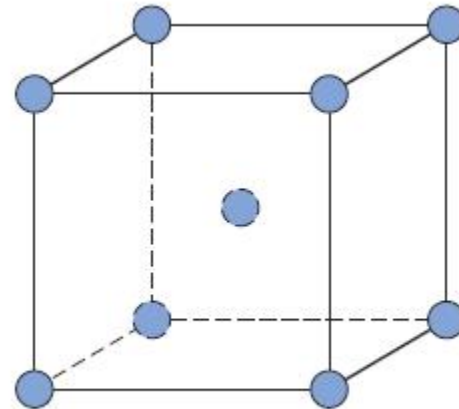
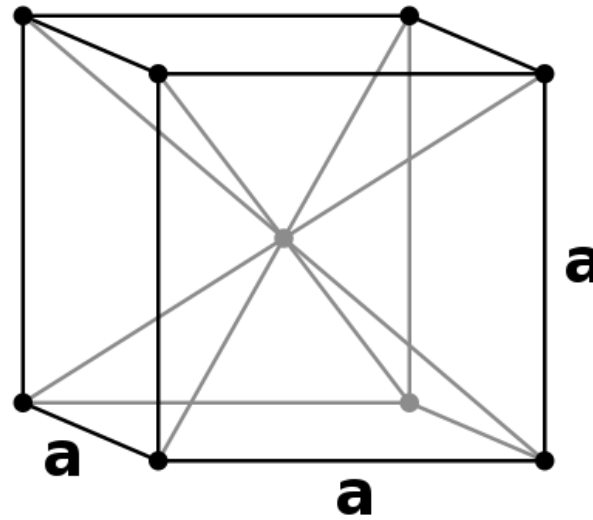
**Auguste Bravais (1811-1863)**

Kübik Yapılar: 3 çeşit

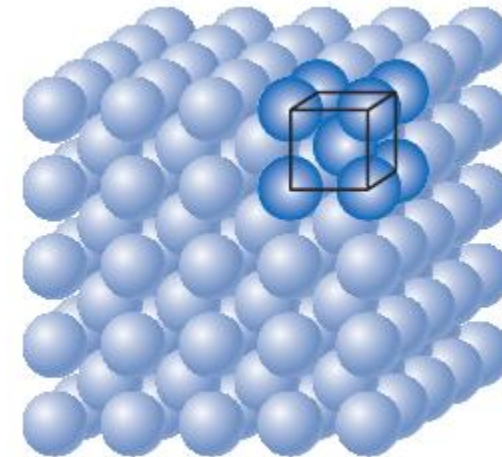
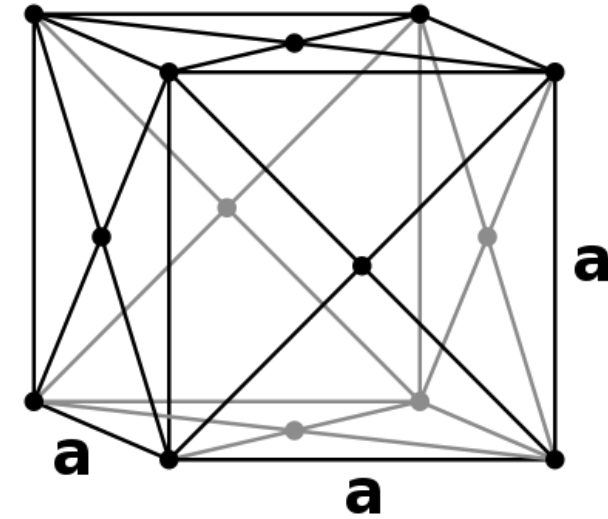
**Basit Kübik**  
Simple Cubic (SC)



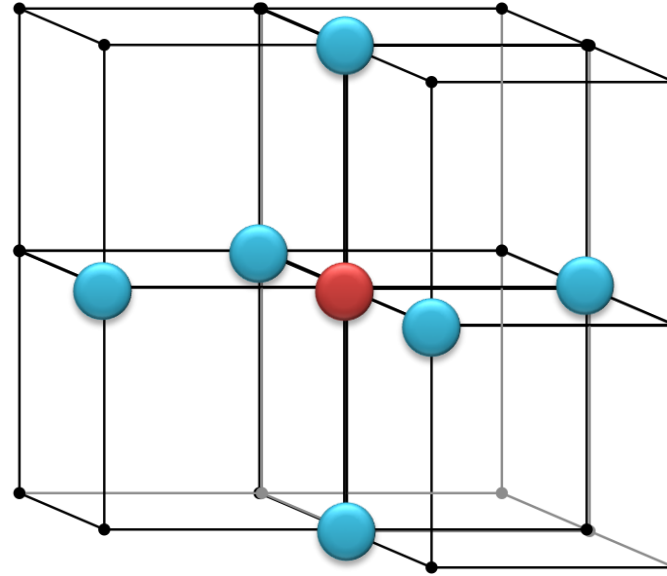
**Hacim Merkezli Kübik**  
Body-Centered Cubic (BCC)



**Yüzey Merkezli Kübik**  
Face-Centered Cubic (FCC)



**Koordinasyon Sayısı (Coordination number):** Metallerde her bir atom aynı sayıda komşu (kendisine değen) atoma sahiptir ve bu sayıya koordinasyon sayısı denir.

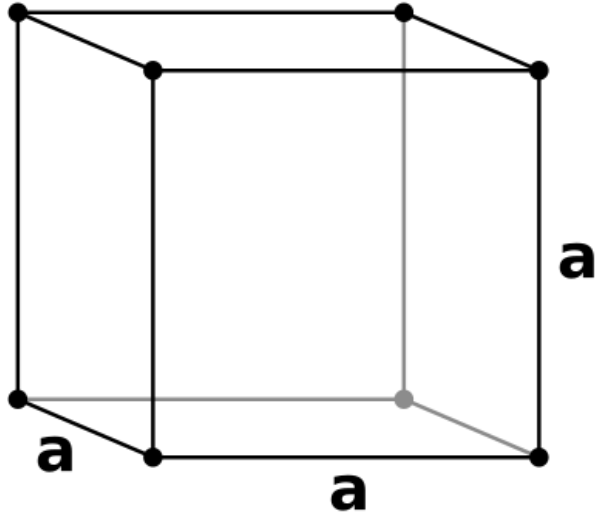


**Atomik paketlenme faktörü (Atomic Packing Factor):** Bir birim hücre içindeki tüm atomların hacimleri toplamının birim hücrenin toplam hacmine oranıdır.

$$APF = \frac{\text{birim hücre içerisindeki toplam atom hacmi}}{\text{birim hücre hacmi}}$$

## Birim hücre hacminin atom yarıçapı cinsinden hesaplanması

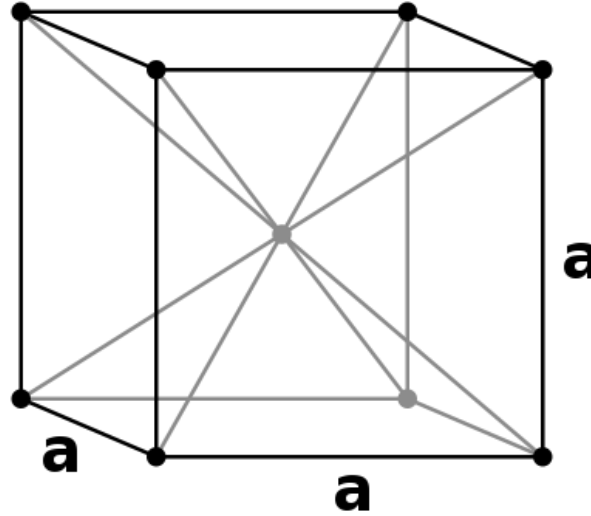
**Basit Kübik (BK)**  
Simple Cubic (SC)



$$a = 2r$$

$$V_{SC} = a^3 = 8r^3$$

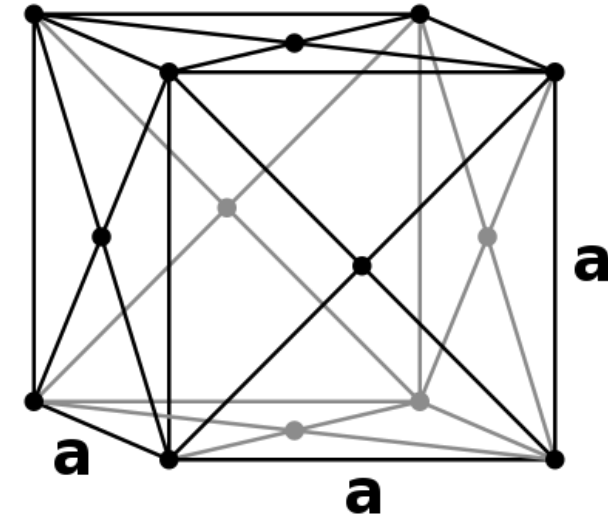
**Hacim Merkezli Kübik (HMK)**  
Body –Centered Cubic (BCC)



$$a = \frac{4r}{\sqrt{3}}$$

$$V_{BCC} = a^3 = \frac{64r^3}{3\sqrt{3}}$$

**Yüzey Merkezli Kübik (YMK)**  
Face –Centered Cubic (FCC)

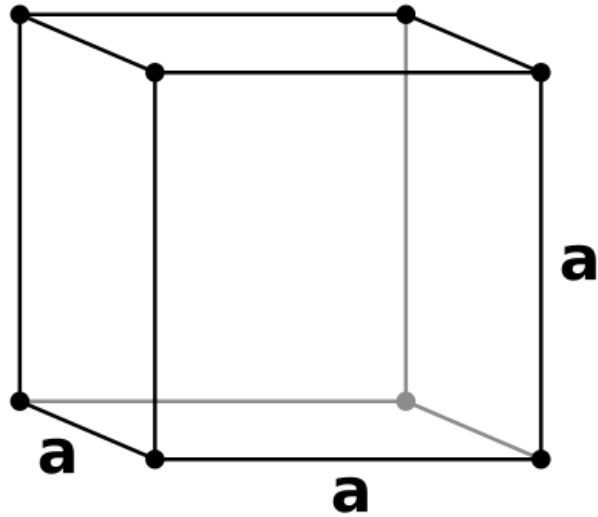


$$a = \frac{4r}{\sqrt{2}}$$

$$V_{FCC} = a^3 = \frac{32r^3}{\sqrt{2}} = 16r^3\sqrt{2}$$

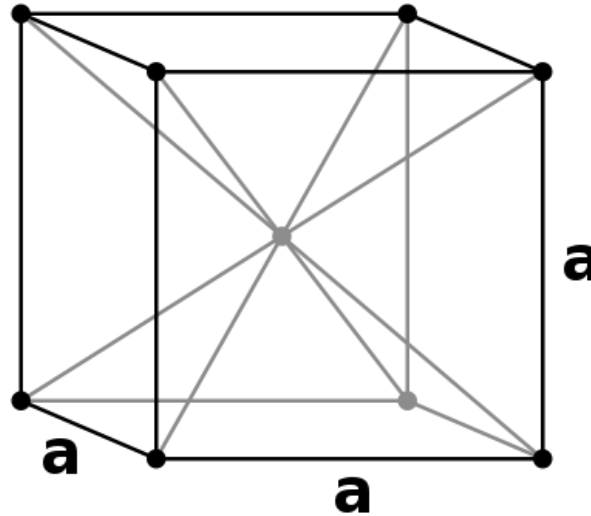
## Birim Hücre İçerisindeki Atom Sayıları

**Basit Kübik**  
Simple Cubic (SC)



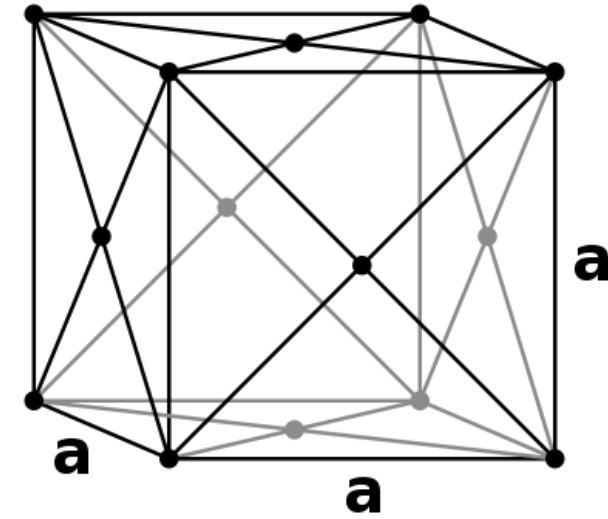
$$N_{SC} = 8 \frac{1}{8} = 1$$

**Hacim Merkezli Kübik**  
Body –Centered Cubic (BCC)



$$N_{BCC} = 1 + 8 \frac{1}{8} = 2$$

**Yüzey Merkezli Kübik**  
Face –Centered Cubic (FCC)



$$N_{FCC} = 6 \frac{1}{2} + 8 \frac{1}{8} = 4$$

**Atomik paketleme faktörü:**  $APF = \frac{\text{birim hücre içerisindeki toplam atom hacmi}}{\text{birim hücre hacmi}}$

**Basit Kübik (BK)**  
Simple Cubic (SC)

$$V_{SC} = a^3 = 8r^3$$

$$N_{SC} = 8 \cdot \frac{1}{8} = 1$$

$$AFP_{SC} = \frac{1 \cdot \frac{4}{3} \pi r^3}{8r^3} = 0.524$$

**Hacim Merkezli Kübik (HMK)**  
Body –Centered Cubic (BCC)

$$V_{BCC} = a^3 = \frac{64r^3}{3\sqrt{3}}$$

$$N_{BCC} = 1 + 8 \cdot \frac{1}{8} = 2$$

$$AFP_{BCC} = \frac{2 \cdot \frac{4}{3} \pi r^3}{\frac{64r^3}{3\sqrt{3}}} = 0.68$$

**Yüzey Merkezli Kübik (YMK)**  
Face –Centered Cubic (FCC)

$$V_{FCC} = a^3 = \frac{32r^3}{\sqrt{2}} = 16r^3\sqrt{2}$$

$$N_{FCC} = 6 \cdot \frac{1}{2} + 8 \cdot \frac{1}{8} = 4$$

$$AFP_{FCC} = \frac{4 \cdot \frac{4}{3} \pi r^3}{16r^3\sqrt{2}} = 0.74$$



# KATILARIN KRİSTAL YAPILARI

Yoğunluk hesaplamaları:  $\rho = \frac{N_{BH} A}{V_{BH} N_{Avagadro}}$

Bakır:

$$r_{Cu} = 0.128 \text{ nm}$$

$$A_{Cu} = 63.5 \text{ g/mol}$$

Kristal Yapısı = FCC

$\rho = \frac{m}{V} \Rightarrow$   ~~$\rho = \frac{m_{Cu}}{V_{Cu}}$~~   ~~$\rho = \frac{m_{Cu}}{\frac{4}{3} \pi (r_{Cu})^3}$~~

$\rho = \frac{m_{\text{Birim hücre}}}{V_{\text{birim hücre}}} = \frac{n \times m_{Cu}}{a^3}$

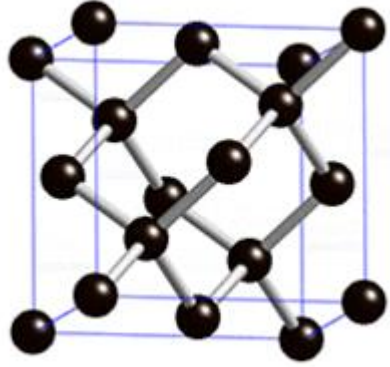
$$V_{FCC} = a^3 = \frac{32r^3}{\sqrt{2}} = 16r^3\sqrt{2}$$

$$N_{FCC} = 6 \frac{1}{2} + 8 \frac{1}{8} = 4$$

$$\rho_{Cu} = \frac{4 \text{ atom/birim hücre} \times 63.5 \text{ g/mol}}{\left[ 16(1.28 \times 10^{-8} \text{ cm})^3 \sqrt{2} \right] / \text{birim hücre} \times 6.022 \times 10^{23} \text{ atom/mol}} = 8.89 \text{ g/cm}^3$$

Avagadro Sayısı = ?

**Silicon:** Elmas kübik (diamond cubic) yapıdadır.



Kafes Parametresi:  $a_{Si} = 0.54310206 \text{ nm}$

Atom Ağırlığı:  $MW_{Si} = 28.0854 \text{ gr / mol}$

Yoğunluk:  $\rho_{Si} = 2.3290 \text{ gr / cm}^3$

$$N_{SC} = 8 \frac{1}{8} + 6 \frac{1}{2} + 4 \frac{1}{1} = 8$$

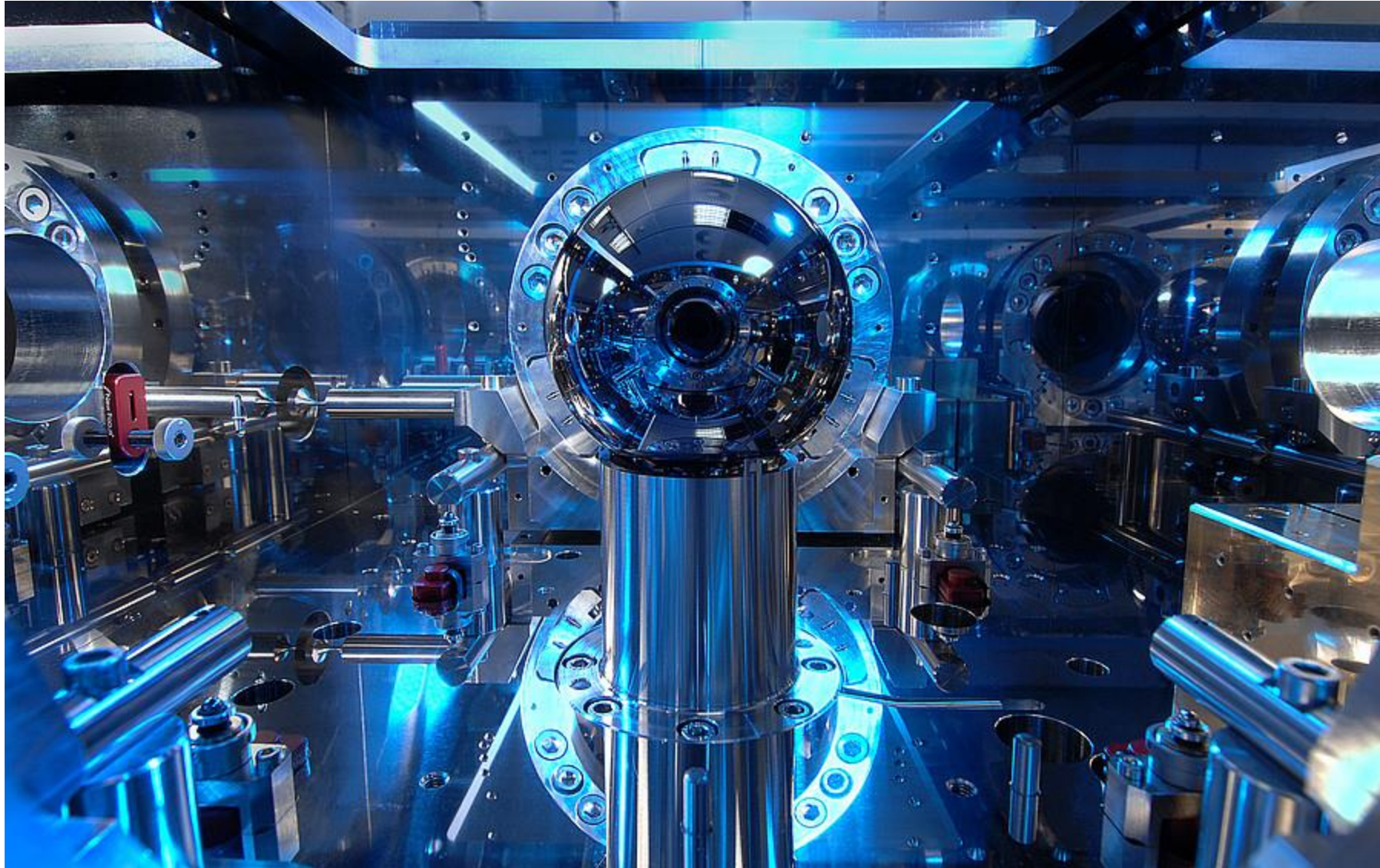
Atom Hacmi:  $AV_{Si} = \frac{(5.4310206 \times 10^{-8} \text{ cm})^3}{\text{atom}}$

Molar Volume:  $MV_{Si} = 12.0589953 \text{ cm}^3 / \text{mol}$

iso	NA	half-life	DM	DE (MeV)	DP
$^{28}\text{Si}$	92.23%	$^{28}\text{Si}$ is stable with 14 neutrons			
$^{29}\text{Si}$	4.67%	$^{29}\text{Si}$ is stable with 15 neutrons			
$^{30}\text{Si}$	3.1%	$^{30}\text{Si}$ is stable with 16 neutrons			
$^{32}\text{Si}$	trace	153 y	$\beta^-$	13.020	$^{32}\text{P}$

$\Rightarrow \frac{MV_{Si}}{AV_{Si}} = 6.02222201 \times 10^{23} \text{ atom / mol}$

Avagadro Sayısı = ?



<https://www.youtube.com/watch?v=ZMByI4s-D-Y>

Avagadro Sayısı = ?

<https://www.youtube.com/watch?v=ZMByl4s-D-Y>

**Silicon:** Elmas kübik (diamond cubic) yapıdadır.



Quantity	Unit	AVO28-S5	AVO28-S8
$a$	pm	543.099 6240(19)	543.099 618 5(20)
$m$	g	1000.087 560(15)	1000.064 543(15)
$V$	cm <sup>3</sup>	431.059 059(13)	431.049 110(10)
$\rho$	kg/m <sup>3</sup>	2320.070 855(76)	2320.071 007(63)
$M$	g/mol	27.976 970 26(22)	27.976 970 29(23)
$N_A$	10 <sup>23</sup> mol <sup>-1</sup>	6.022 140 91(21)	6.022 140 71(18)

$$\rightarrow \frac{MV_{Si}}{AV_{Si}} = 6.02214078(18) \times 10^{23} \text{ atom / mol}$$

Quantity	Relative Uncertainty (10 <sup>-9</sup> )	Contribution (%)
Molar Mass	6	4
Sphere Mass	3	1
Surface	15	24
Sphere Volume	23	57
Lattice Parameter	11	13
Crystal Perfection	3	1

1 kilogram tek-kristal silikon küre

<sup>28</sup>Si izotopu zenginleştirilmiş

*International Avogadro Coordination*

*Russian Academy of Sciences,  
Nizhny-Novgorod, Russia, 2007.*

# KRİSTAL GEOMETRİLERİ

**Polimorfizm:** Bazı metal ve ametallerin birden fazla kristal yapıya sahip olmasına denir.

**Allotropi:** Elemental katılarda gözlenen polimorfizm genellikle allotropi olarak adlandırılır.

Kristal yapı *basınç* ve *sıcaklığa* bağlıdır.

**Karbon:**

*Grafit:* normal ortam koşullarında bulunan kararlı polimorf



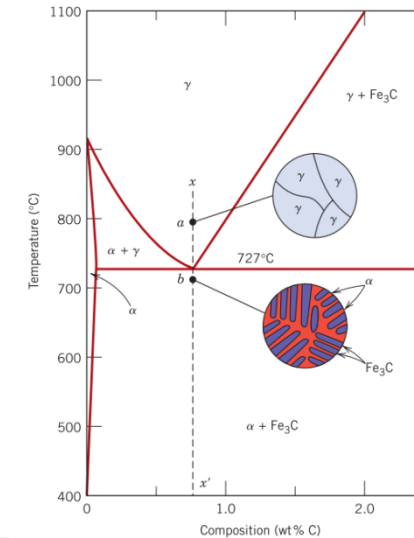
*Elmas:* çok yüksek basınç altında oluşur



**Demir:**

*BCC:* normal ortam koşullarında bulunur

*FCC:* 912 °C'de BCC =>FCC dönüşümü olur



## Allotropik Dönüşüm:

*Roald Amundsen*

Norveçli kutup araştırmacısı



*Robert Scott*

İngiliz kutup araştırmacısı



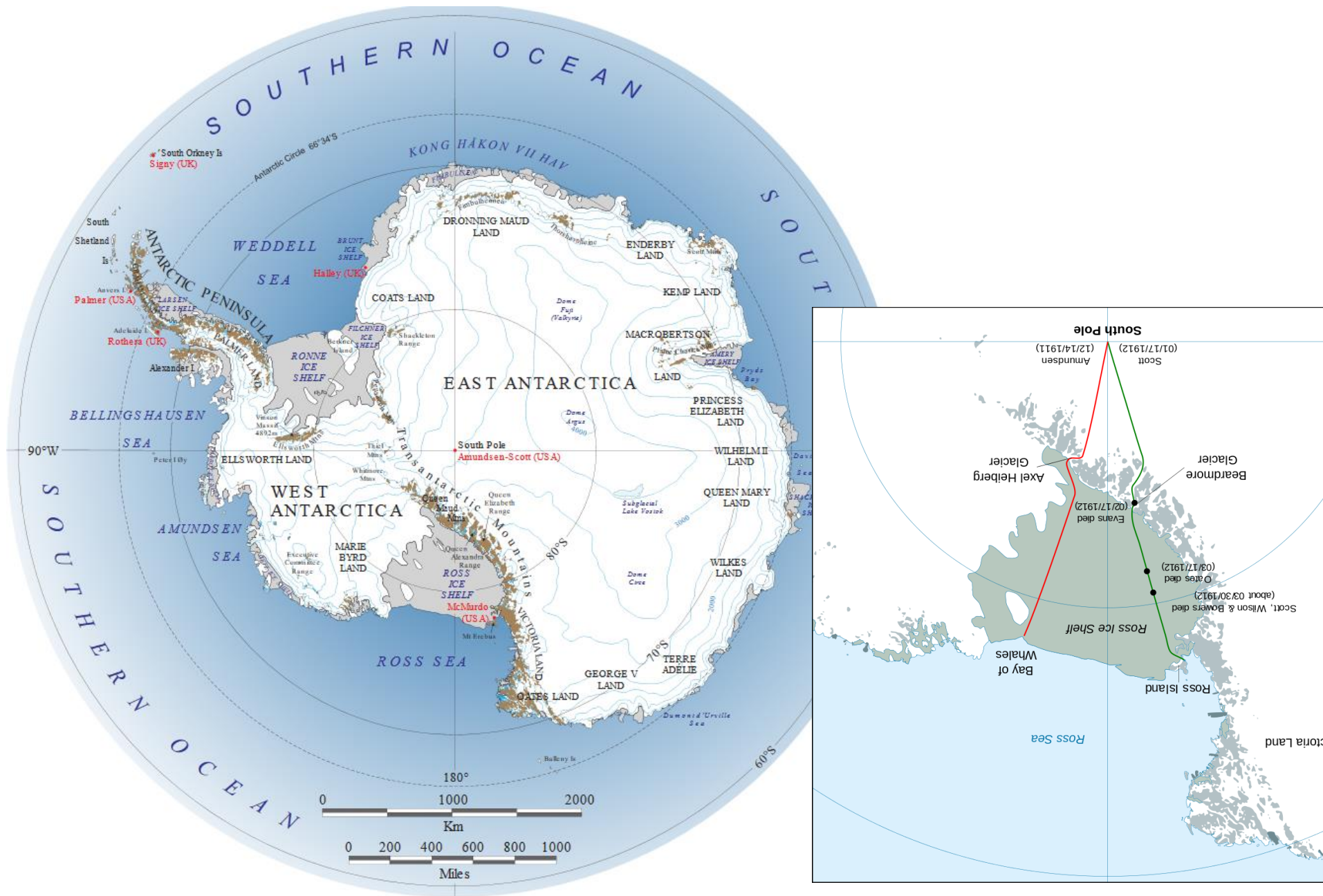
*Amundsen-Scott İstasyonu*



29 March 1912

B. T. Brooks, 'Tin Disease and Polar Exploration' *Science*, **40**, 166-167 (1914).

# KRISTAL GEOMETRİLERİ



B. T. Brooks, 'Tin Disease and Polar Exploration' *Science*, **40**, 166-167 (1914).

In Scott's diary<sup>1</sup> of the return journey under date of February 24, 1912, he states:

Found store in order except shortage oil—shall have to be *very* saving with fuel—. . . . Wish we had more fuel.

Again on February 26 he states:

The fuel shortage still an anxiety. . . . Fuel is woefully short.

March 4:

We can expect little from man now except the possibility of extra food at the next depot. It will be real bad if we get there and find the same shortage of oil.

On March 7:

If there is a shortage of oil again we can have little hope.

### Kurtarma Operasyonu Notları

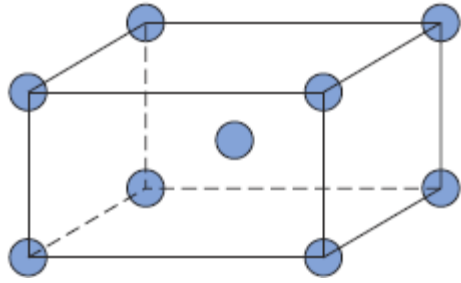
2. When the search party reached One Ton Camp in November, 1912, they found that some of the food, stacked in a canvas "tank" at the foot of the cairn, was quite oily from the spontaneous leakage of the tins seven feet above it on the top of the cairn.

### Sonuç

seems impossible. A possible and very plausible explanation of this leakage of oil is the conversion of ordinary tin into the allotropic form, gray tin powder. This change to gray tin powder is known to take place at a maximum rate at  $-48^{\circ}$  C. and may take place more slowly at other temperatures below  $18^{\circ}$  C. Should this change occur along the soldered seams of the container, the mysterious leakage of oil might well be explained. This peculiar disintegration of tin is also shown by certain alloys of tin. Articles of pewter (tin 4 parts, lead one part) have frequently been known to show such changes and this change has indeed been given the name "museum disease," referring to pewter articles. Farup<sup>2</sup>



## Allotropik Dönüşüm:



Hacim Merkezli  
Tetragonal

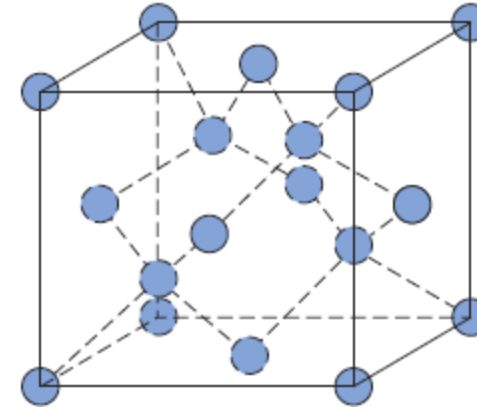
$$\rho_{Sn} = 7.30 \text{ g} / \text{cm}^3$$

## Kalay (Sn) Hastalığı

13.2 °C



Soğutma



Elmas Kübik

$$\rho_{Sn} = 5.77 \text{ g} / \text{cm}^3$$



% 27 Hacim Artışı



antimon (Sb) veya  
bizmut (Sb) ilavesiyle  
önlenebilir

[https://www.youtube.com/watch?v=sXB83Heh3\\_c](https://www.youtube.com/watch?v=sXB83Heh3_c)

**Önümüzdeki Ders Saatinde**

**Ders Kitabımızın 3. Bölümündeki**

**KRİSTAL GEOMETRİLERİ,  
KRİSTALOGRAFİK YÖNLER VE DÜZLEMLER**

**adlı konuya başlayacağız!**