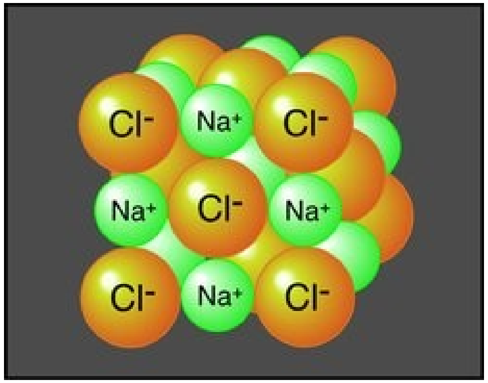
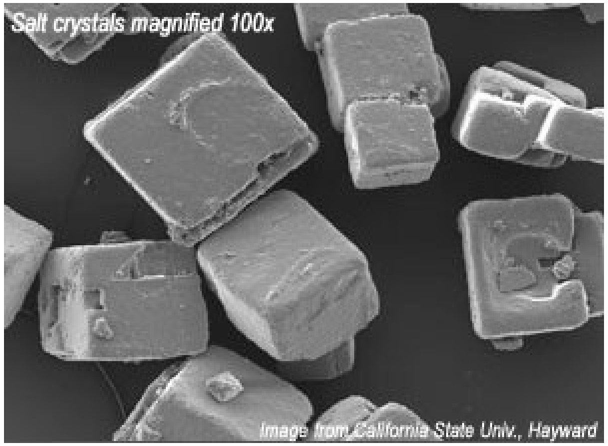
Materiais Cristalinos

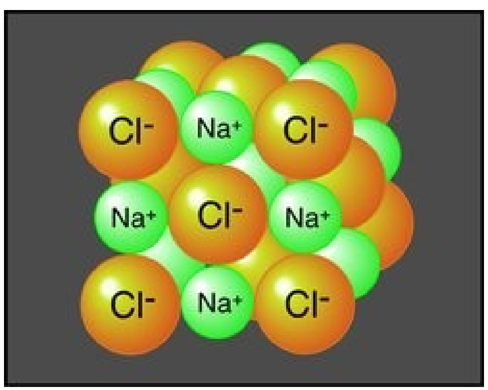
- **Ligações atômicas nos cristais.**
  - **Cristais iônicos.**
  - **Cristais covalentes.**
  - **Cristais moleculares.**
  - **Metais.**
  - **Cristais com ligações de hidrogênio.**



Ligações atômicas em cristais

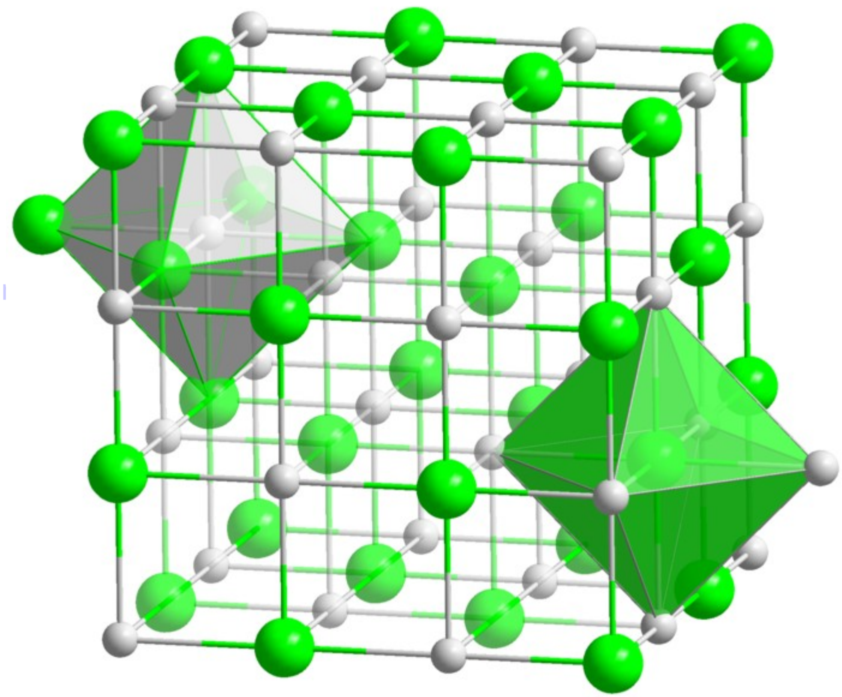


http://www.middleschoolchemistry.com/multimedia/chapter4/lesso



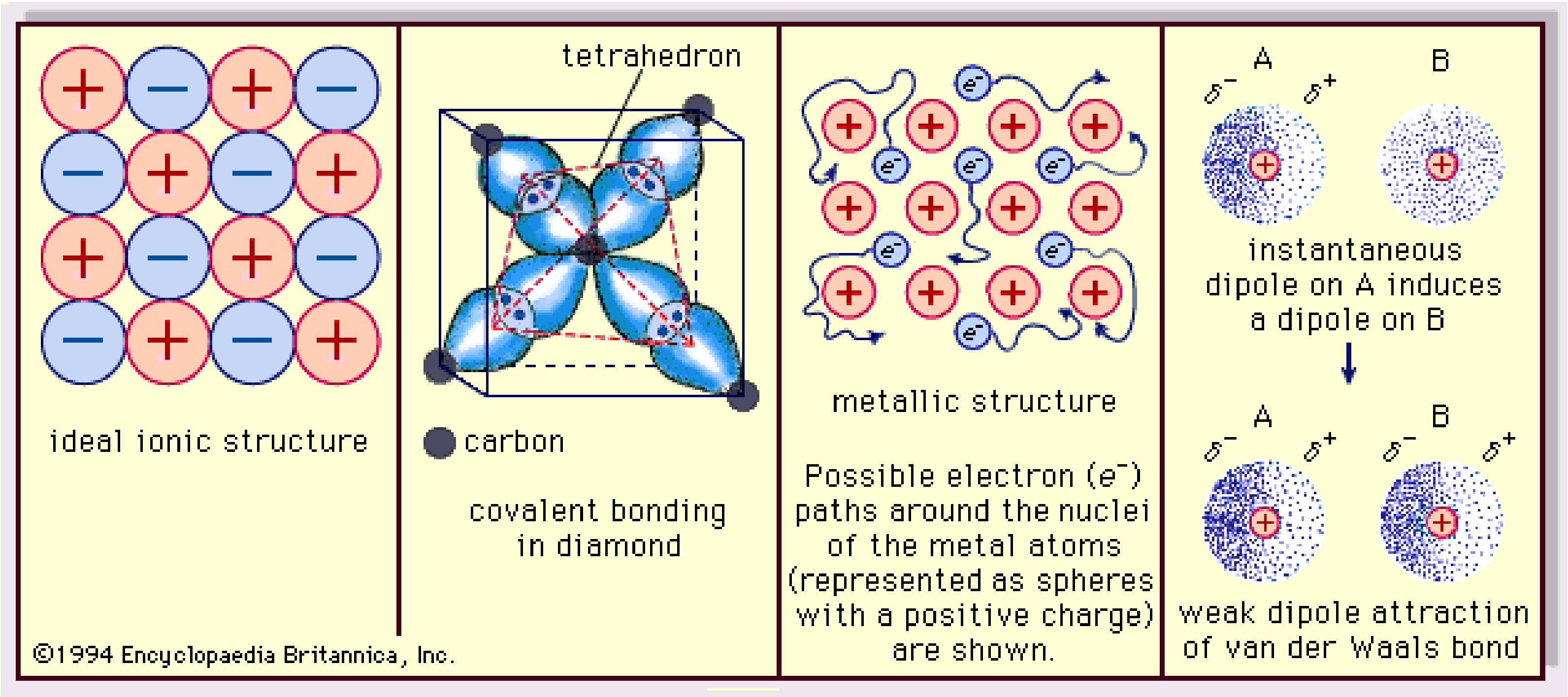
http://www.eoearth.org/article/Matter

Exemplo: cristal de NaCl



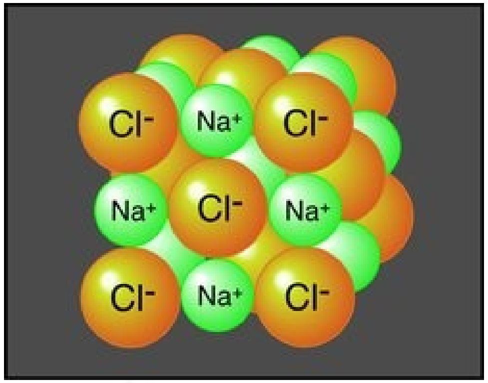
http://en.wikipedia.org/wiki/Sodium_chloride

Ligações atômicas em cristais



Ligação iônica **Ligação covalente** **Ligação metálica** **Ligação molecular**

Ligações atômicas em cristais



http://www.eoearth.org/article/Matter

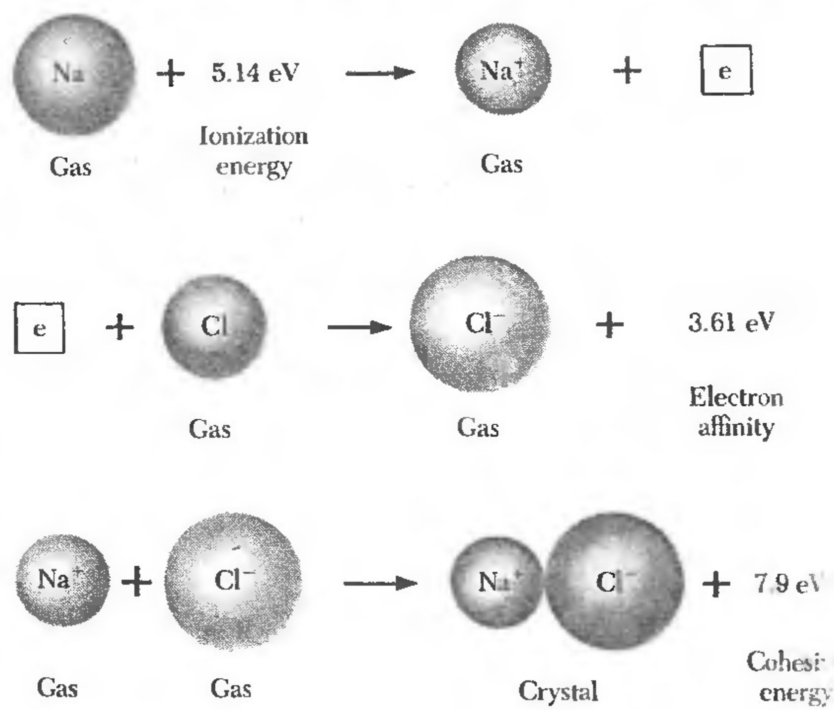


Figure 8 The energy per molecule unit of a crystal of sodium chloride is $(7.9 - 5.1 + 3.6) = 6.4$ eV lower than the energy of separated neutral atoms. The lattice energy with respect to separated ions is 7.9 eV per molecule unit. All values on the figure are experimental. Values of the ionization energy are given in Table 5, and values of the electron affinity are given in Table 6.

Introduction to Solid State Physics, Kittel, 1996.

Ligações atômicas em cristais

Ligação iônica - modelo para energia potencial:

$$U(R) = N(\gamma e^{-R/\rho} - \alpha q^2 / R)$$

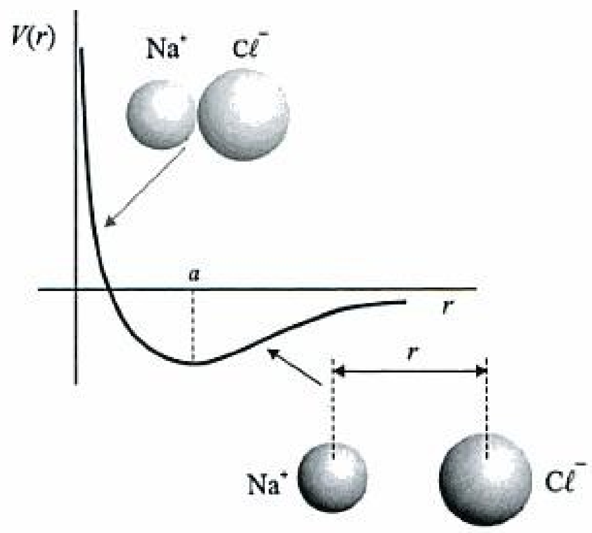


Figura 1.1: Energia de interação efetiva entre um íon Na^+ e um íon $C\ell^-$ em função da distância entre seus núcleos.

NaCl (fcc):

$$\gamma = 1{,}05 \times 10^{-15}\ \mathrm{J}$$

$$\rho = 0{,}321\ \text{Å}$$

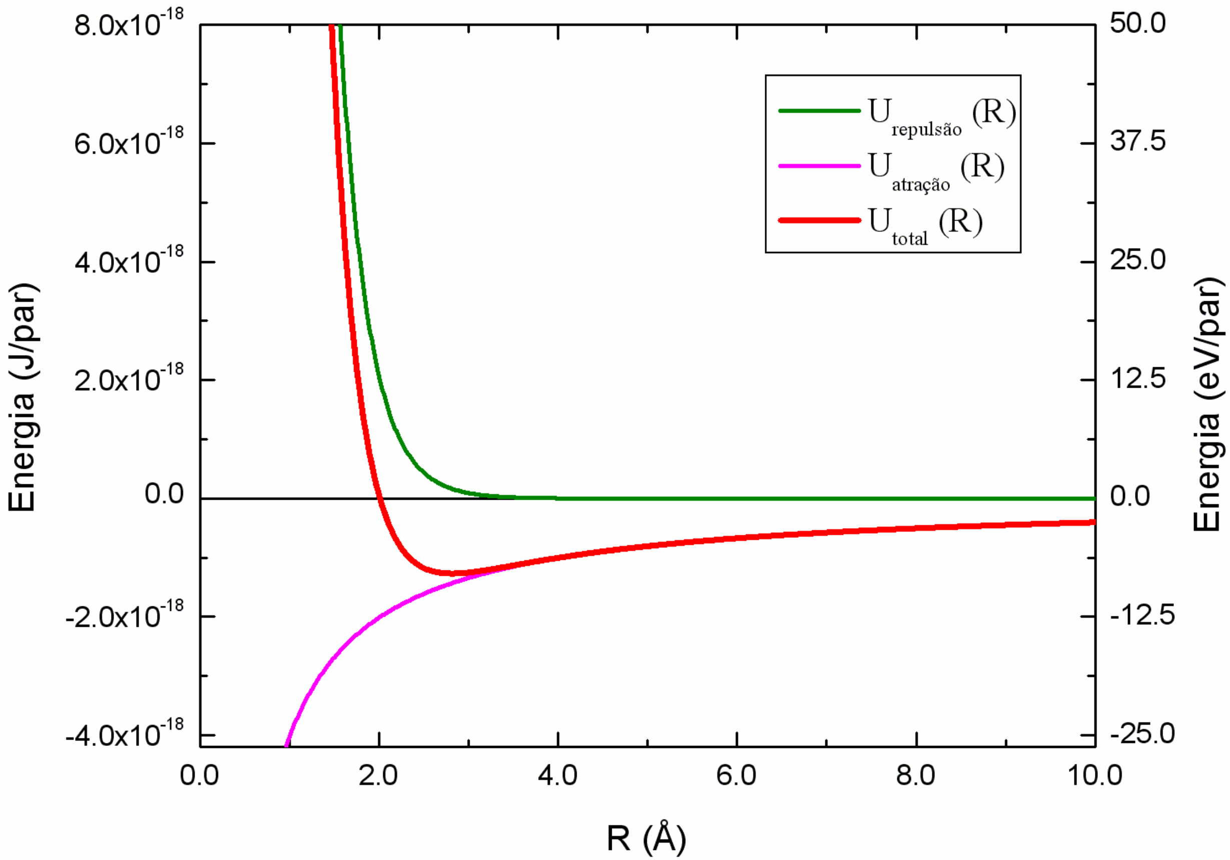
$$\alpha = 1{,}747 / 4\pi\varepsilon_0$$

$$q = 1{,}602 \times 10^{-19}\ \mathrm{C}$$

Materiais e Dispositivos Eletrônicos, Sérgio M. Rezende, 2004.

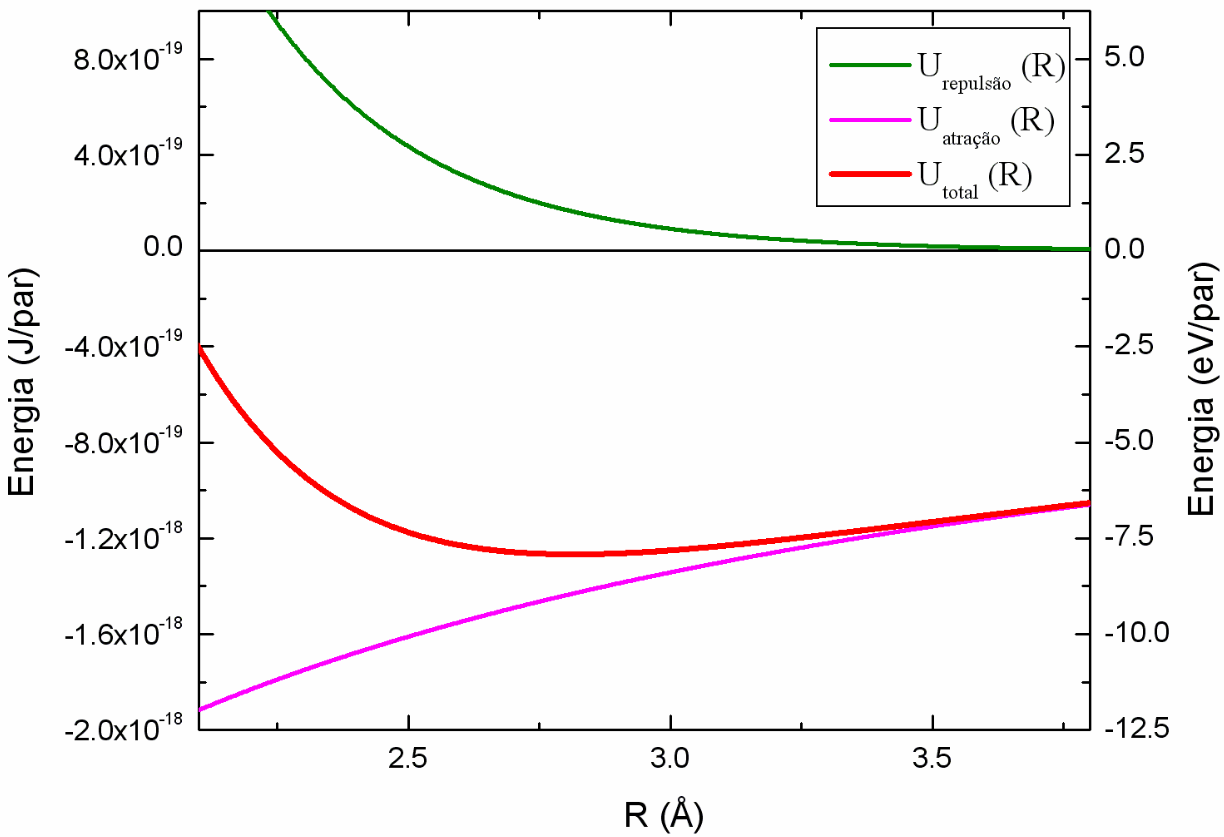
Ligações atômicas em cristais

$$U(R) = N(\gamma e^{-R/\rho} - \alpha q^2 / R)$$



Ligações atômicas em cristais

$$U(R) = N(\gamma e^{-R/\rho} - \alpha q^2 / R)$$



Ligações atômicas em cristais

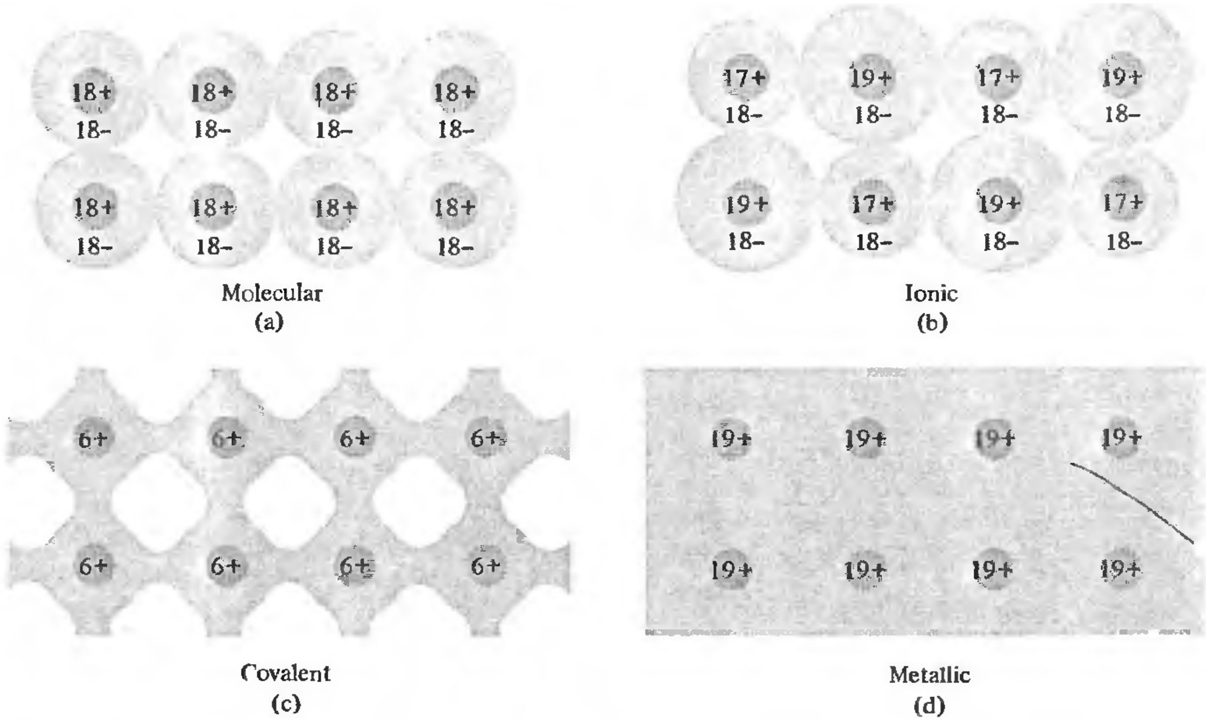


Figure 19.3
Highly schematic two-dimensional representation of the electronic charge distribution in the basic solid types. The small circles represent the positively charged nuclei, and the shaded parts, regions in which the electronic density is appreciable (though by no means uniform). We have (a) molecular (represented by two-dimensional "argon"): (b) ionic ("potassium chloride"); (c) covalent ("carbon"); (d) metallic ("potassium").

Solid State Physics, Ashcroft / Mermin, 1976.

Ligações atômicas em cristais

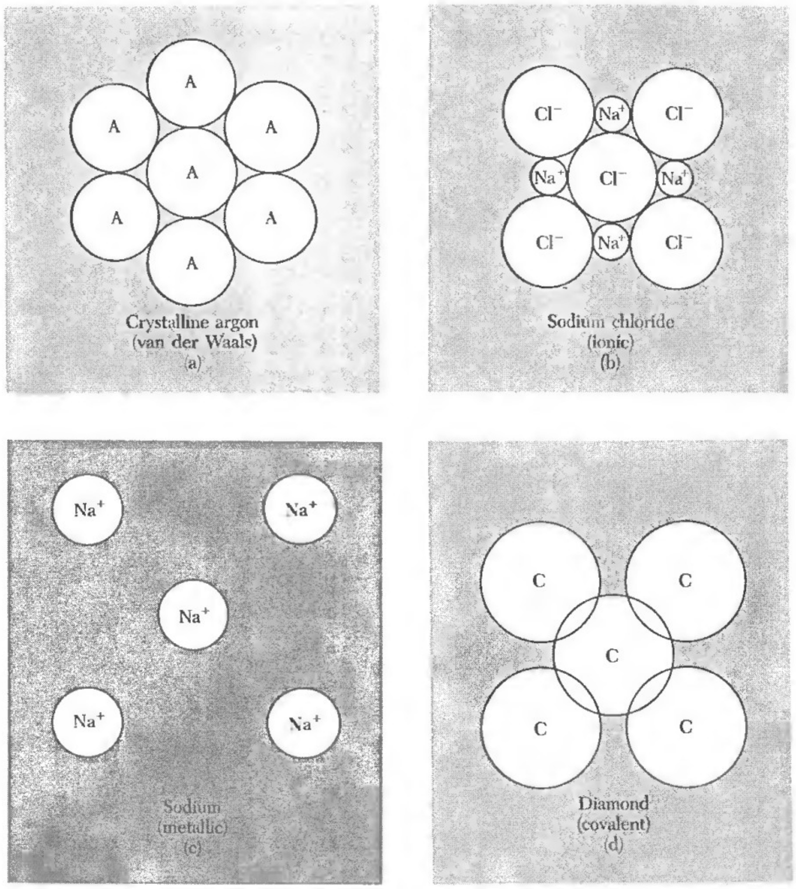


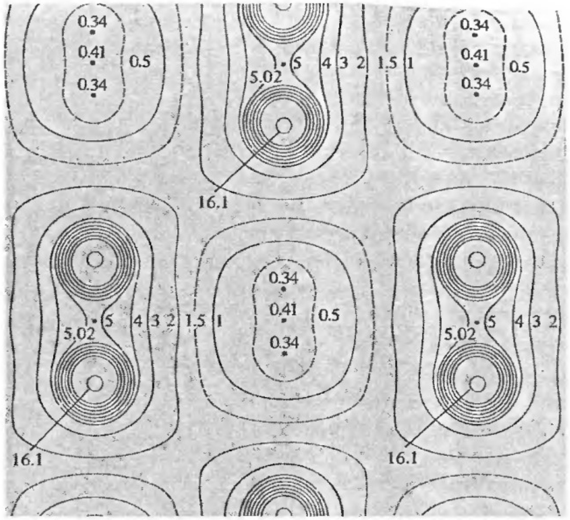
Figure 1 The principal types of crystalline binding. In (a) neutral atoms with closed electron shells are bound together weakly by the van der Waals forces associated with fluctuations in the charge distributions. In (b) electrons are transferred from the alkali atoms to the halogen atoms, and the resulting ions are held together by attractive electrostatic forces between the positive and negative ions. In (c) the valence electrons are taken away from each alkali atom to form a communal electron sea in which the positive ions are dispersed. In (d) the neutral ato[illegible] ppear to be bound together by the overlapping parts of their electron distributions.

Introduction to Solid State Physics, Kittel, 1996.

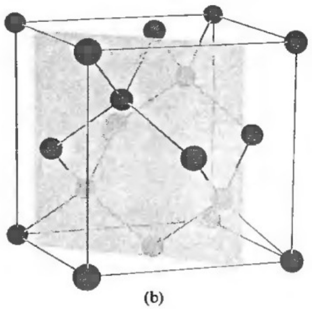
Cristais covalentes e iônicos

Ligação covalente

Figure 19.2
The electronic charge distribution on a plane section of the conventional cubic cell of diamond, as suggested by X-ray diffraction data. The curves in (a) are curves of constant electronic density. The numbers along the curves indicate electronic density in electrons per cubic angstrom. The plane section of the cell that (a) describes is displayed in (b). Note that the electron density is quite high (5.02 electrons per cubic angstrom, as compared with 0.034 in the regions of lowest density) at the points where the plane intersects the nearest neighbor bonds. This is characteristic of covalent crystals. (Based on a figure from Y. K. Syrkin and M. E. Dyatkina, *Structure of Molecules and the Chemical Bond*, translated and revised by M. A. Partridge and D. O. Jordan, Interscience, New York, 1950.)



(a)



(b)

Ligação iônica

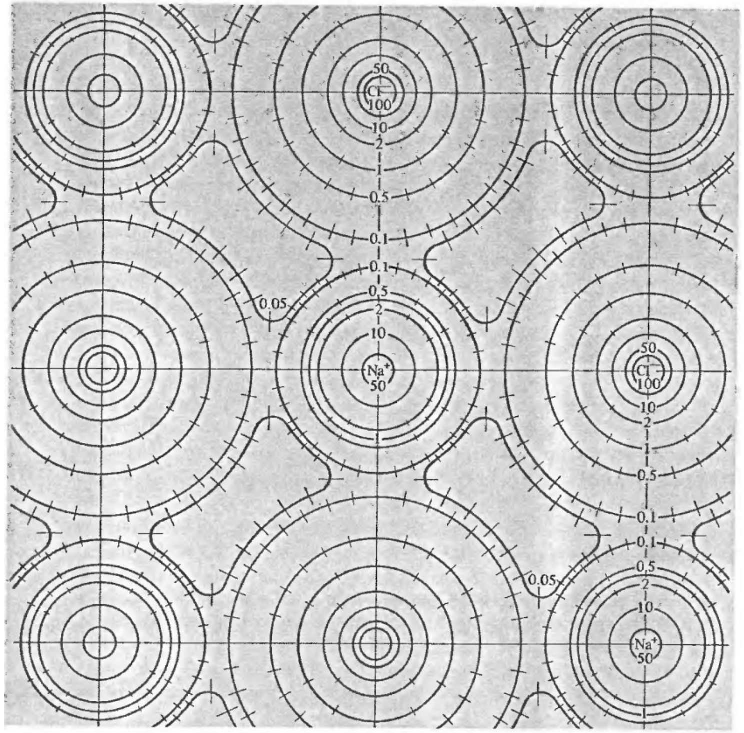


Figure 19.5
Electronic charge density in a [100] plane of NaCl containing the ions, as inferred from X-ray diffraction data. The numbers give the values of the density along lines of constant density, in units of electrons per cubic angstrom. The lines perpendicular to the constant density curves are error bars. (After G. Schoknecht, *Z. Naturforschung* **12**, 983 (1957).)

Solid State Physics, Ashcroft / Mermin, 1976.

Cristais covalentes e iônicos

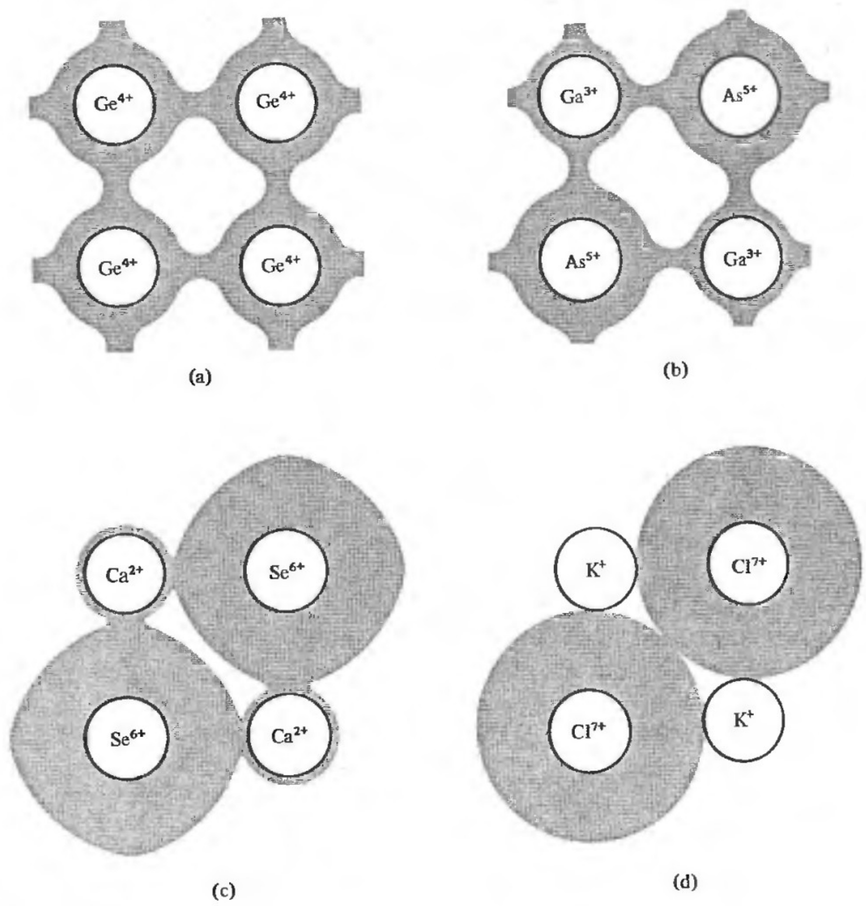
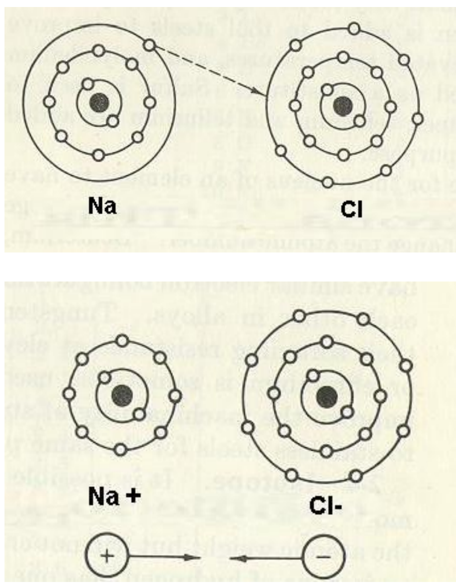


Figure 19.10
A highly schematic representation of the continuity from perfect covalent to perfect ionic crystals. (a) *Perfectly covalent germanium.* Four electrons per unit cell are identically distributed about the Ge^{4+} ion cores. The electronic density is large in certain directions in the interstitial region. (b) *Covalent gallium arsenide.* The interstitial electron density has diminished somewhat and there is a slight tendency for the cloud of electrons around each As^{5+} ion core to have somewhat more charge than is necessary to compensate the positive charge, while the electron cloud around each Ga^{3+} ion core has somewhat less. The crystal thus has a very slight ionic character as well. (c) *Ionic calcium selenide.* The Ca^{2+} ion is almost denuded of valence electrons and the cloud of electrons around the Se^{6+} ion core is almost the full eight necessary to produce Se^{--}. (It would be more conventional, in fact, to represent the selenium as an Se^{--} ion core lacking a small fraction of an electron.) The crystal is weakly covalent, to the extent that the Ca^{2+} is slightly shielded by electrons in its immediate neighborhood, and the Se^{6+} does not have quite enough electrons to filled the outer eight shells completely, making Se^{--}. The covalent character is also seen in the slight distortion of the charge distribution outward along nearest-neighbor lines. (d) *Perfectly ionic potassium chloride.* The K^+ ion is bare of excess electrons, and all eight electrons cluster around the Cl^{7+} to make Cl^-. (It would be more conventional to show no electrons at all, and simply draw a Cl^- ion core for the chlorine.)

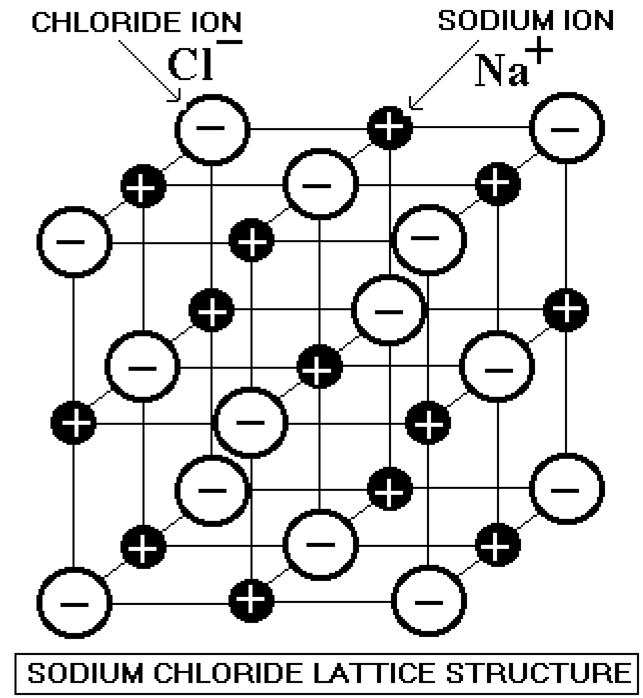
Solid State Physics, Ashcroft / Mermin, 1976.

Cristais iônicos

- Ligação forte – interação eletrostática atrativa entre íons.
- Elétrons altamente localizados em torno dos íons.
- Materiais com ponto de fusão bastante alto.
- Baixa condutividade térmica e elétrica, alta transparência ótica.
- Exemplos: NaCl, KCl, LiF, óxidos, ...



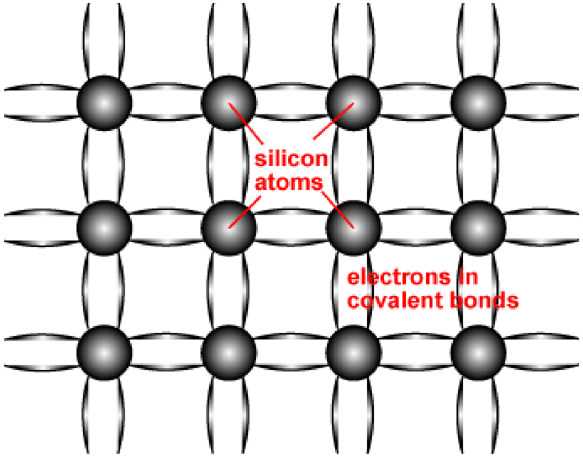
http://info.lu.farmingdale.edu/depts/met/met205/atomicbonds.html



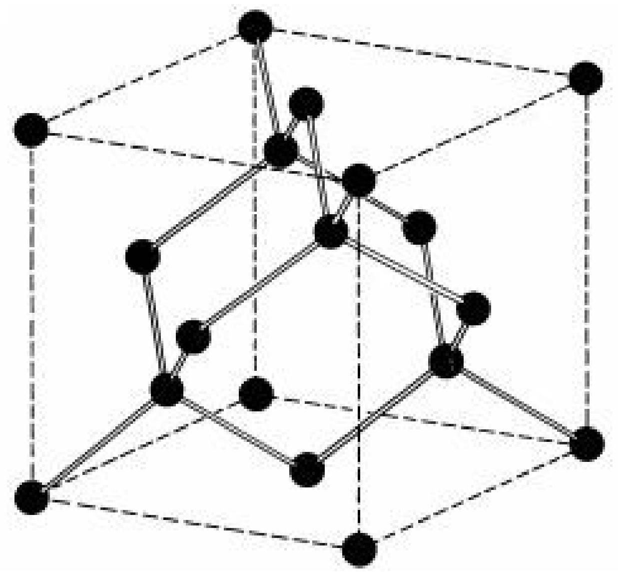
http://www.docbrown.info/page04/4_72bond2.htm

Cristais covalentes

- Densidade eletrônica na região intersticial (entre os átomos no cristal).
- Materiais duros, com ponto de fusão relativamente alto, mas menor que para os cristais iônicos.
- Tipo de ligação mais comum em materiais semicondutores.
- Exemplos: C (diamante), Si, Ge, GaAs, InSb, ...



http://www.asdn.net/asdn/physics/semiconductor.shtml

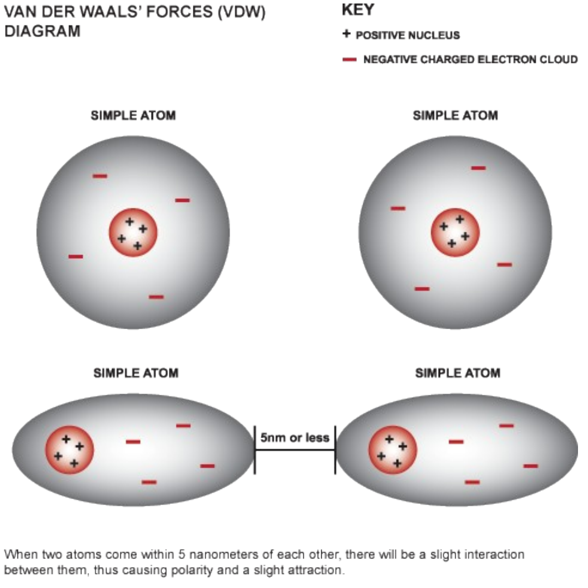


https://code.ua.pt/projects/111/wiki/52_Description_of_Photovoltaic_Elements

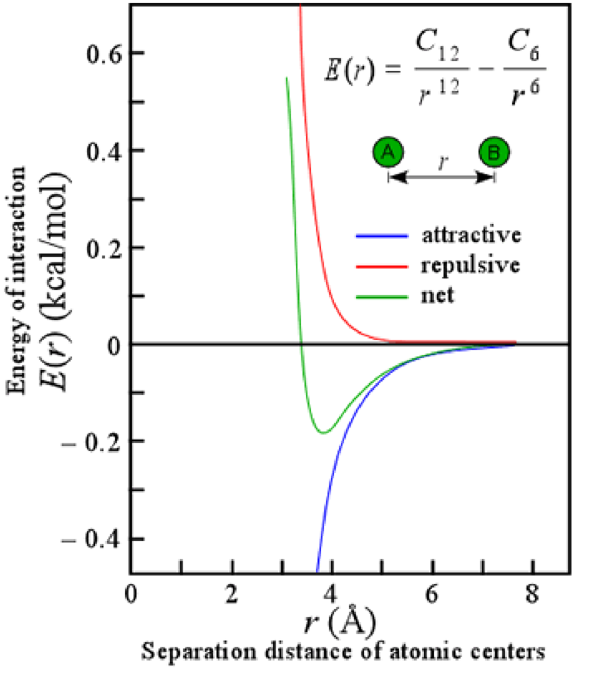
Cristais moleculares

- Interação atrativa: van der Waals (fraca).
- Elétrons localizados nos átomos.
- Ponto de fusão em geral muito baixo (< 100K).
- Exemplos: Ne, Ar, Kr, Xe, O_2, N_2, ...

Interação de van der Waals:



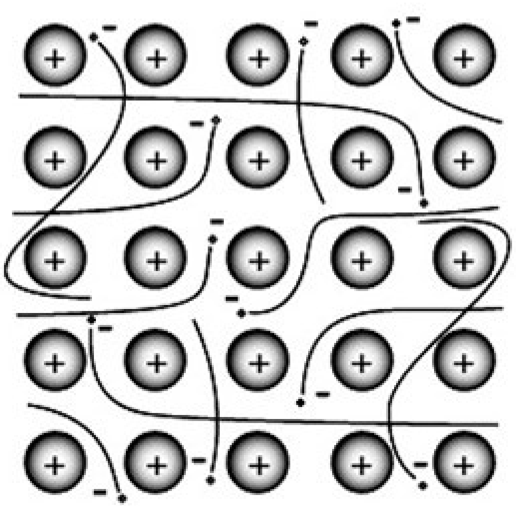
http://www.agpa.uakron.edu/p16/lesson.php?id=hold_on_tight&pg=content

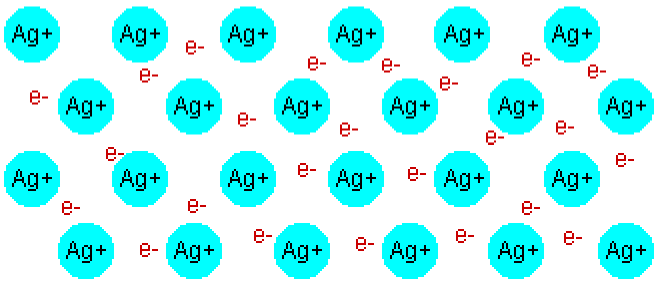


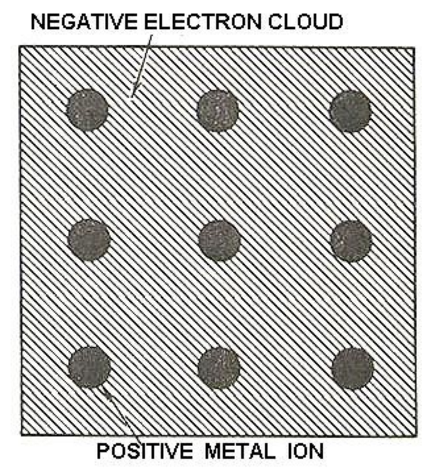
http://guweb2.gonzaga.edu/faculty/cronk/biochem/V-index.cfm?definition=van_der_Waals

Metais

- Elétrons altamente deslocalizados.
- Modelo: “gás de elétrons”, “gás de Fermi”.
- Ligação razoavelmente fraca.
- Ponto de fusão relativamente baixo, grande condutividade elétrica e térmica.
- Exemplos: Li, Na, K, Cu, Ag,...





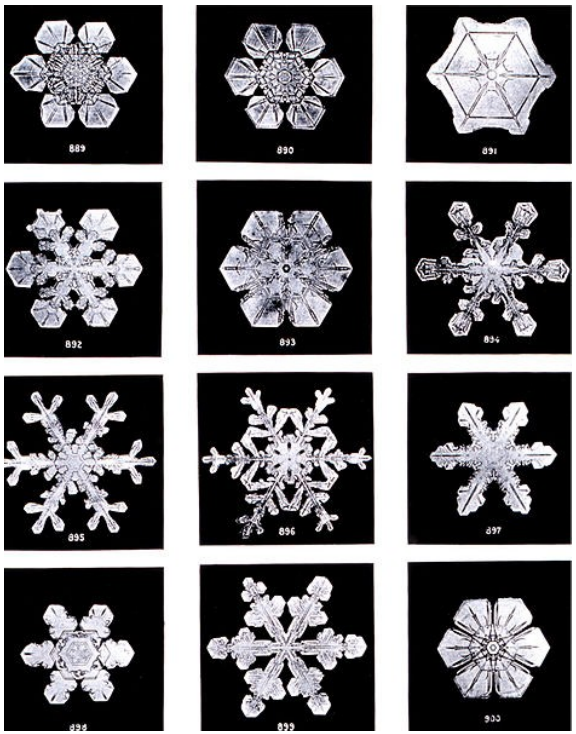


http://www4.nau.edu/meteorite/meteorite/book-glossarym.html

http://info.lu.farmingdale.edu/depts/met/met205/atomicbonds.html

Cristais com ligações de hidrogênio

- “Pontes de hidrogênio”.
- Ligação mais fraca que a iônica ou a covalente, mas mais forte que a interação de van der Waals.
- Exemplos: H_2O (gelo), DNA, polímeros, ...



http://en.wikipedia.org/wiki/Ice

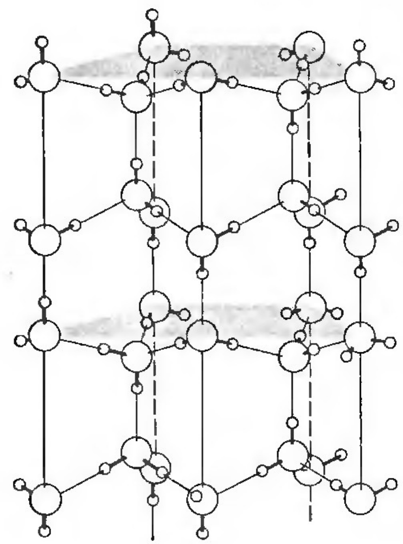
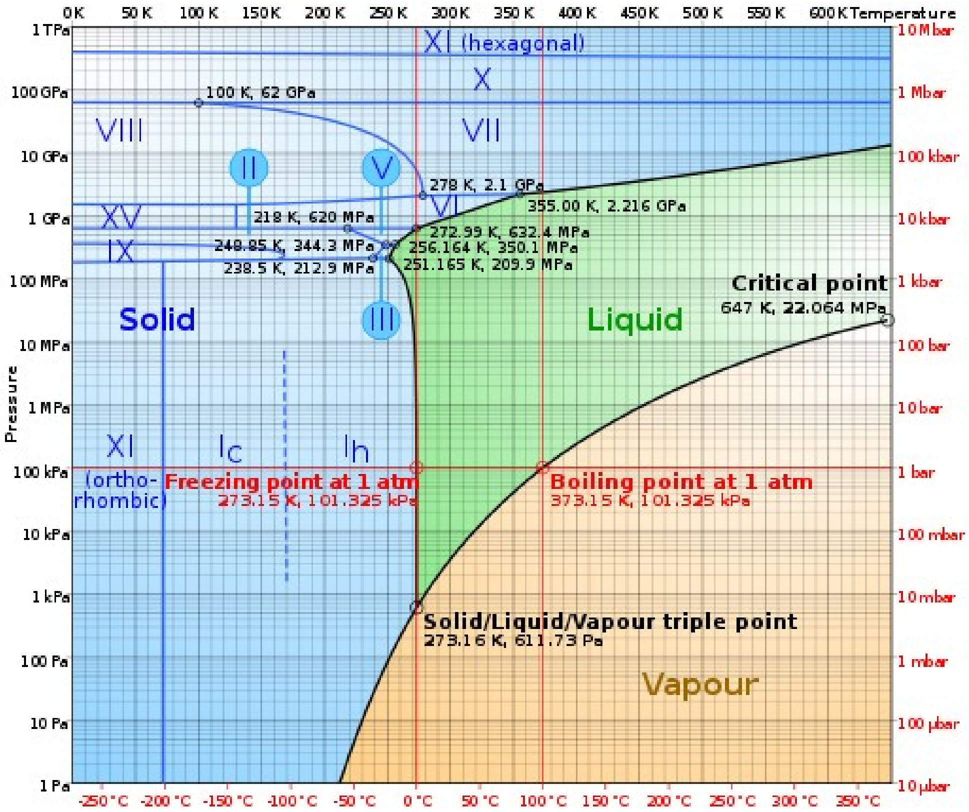


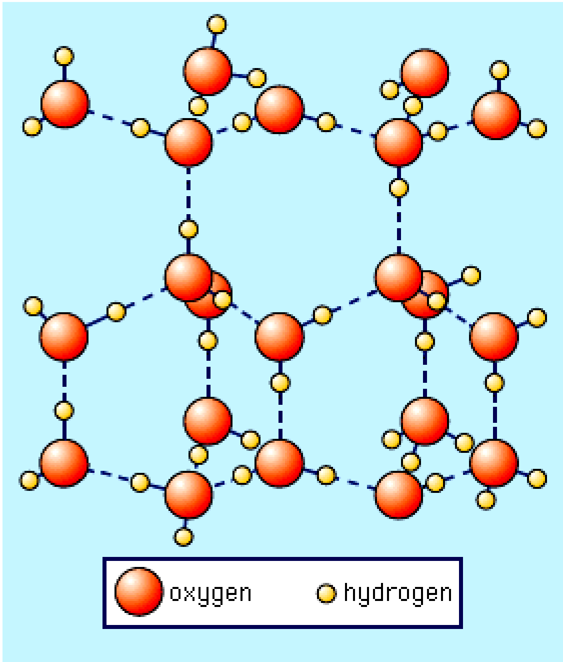
Figure 19.11
The crystal structure of one of the many phases of ice. The large circles are oxygen ions; the small circles are protons. Ice is an example in which hydrogen bonding plays a crucial role. (After L. Pauling, *The Nature of The Chemical Bond*, 3rd. ed., Cornell University Press, Ithaca, New York, 1960.)

Solid State Physics, Ashcroft / Mermin, 1976.

Cristais com ligações de hidrogênio



http://en.wikipedia.org/wiki/Ice



http://www.valdostamuseum.org/hamsmith/Sets2Quarks5.html

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- “*Física do Estado Sólido*”, N. W. Ashcroft, N. D. Mermin. São Paulo: Cengage (2011).
- “*Introdução à Física do Estado Sólido*”, C. Kittel. 8ª edição, Rio de Janeiro: LTC (2005).