Problem 1: Shown on the next page is the crystal structure of the compound ZrO_2. The structure is characterized by an fcc arrangement of the Zr ions, with the O ions located in tetrahedral interstitial sites.

(a) (10 points) Assuming that the bonding is ionic, what is the charge and electronic configuration of the Zr and O ions in this compound (a periodic table is given on the last page of the exam)?

Zr^{4+}: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$

O^{2-}: $1s^2 2s^2 2p^6$

(b) (10 points) Below the figure on the next page, draw the pattern of O and Zr ions in a (110) plane of the crystal structure. Indicate which of the following is the composition within this plane:

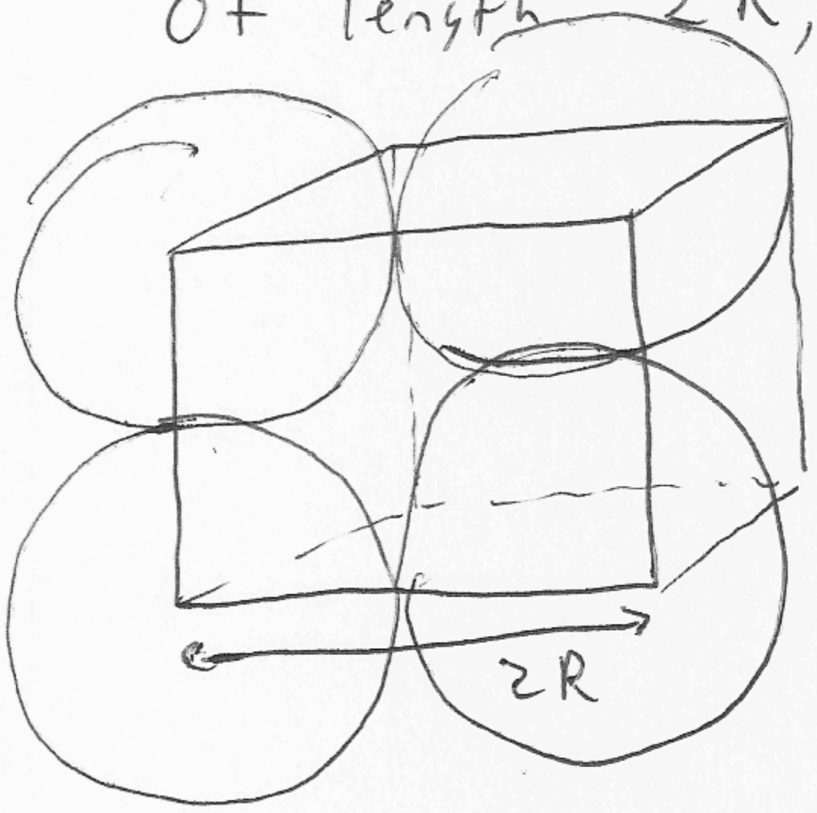
a. ZrO_2
b. ZrO
c. Zr

(c) (10 points) Starting from a Zr ion, which of the following is the sequence of ion types that is encountered as one moves along a [100] and [113] direction in the crystal? Label the direction next to the correct sequence below, and explain your answer by drawing the directions on the figure on the next page.

a. Zr O O Zr O O Zr … [113]
b. Zr Zr Zr Zr Zr Zr … [100]
c. Zr O Zr O Zr O Zr O …
d. Zr Zr O Zr Zr O Zr Zr …

(d) (15 points) The radius of a Zr ion is 0.84 Å and the radius of an O ion is 1.38 Å. What is the radius of the largest atom that would fit in the octahedral interstitial position (located at ½½½) without overlapping with the neighboring atoms?

Octahedral position sits at middle of cube of length 2R, where R = 1.38Å is radius of O.



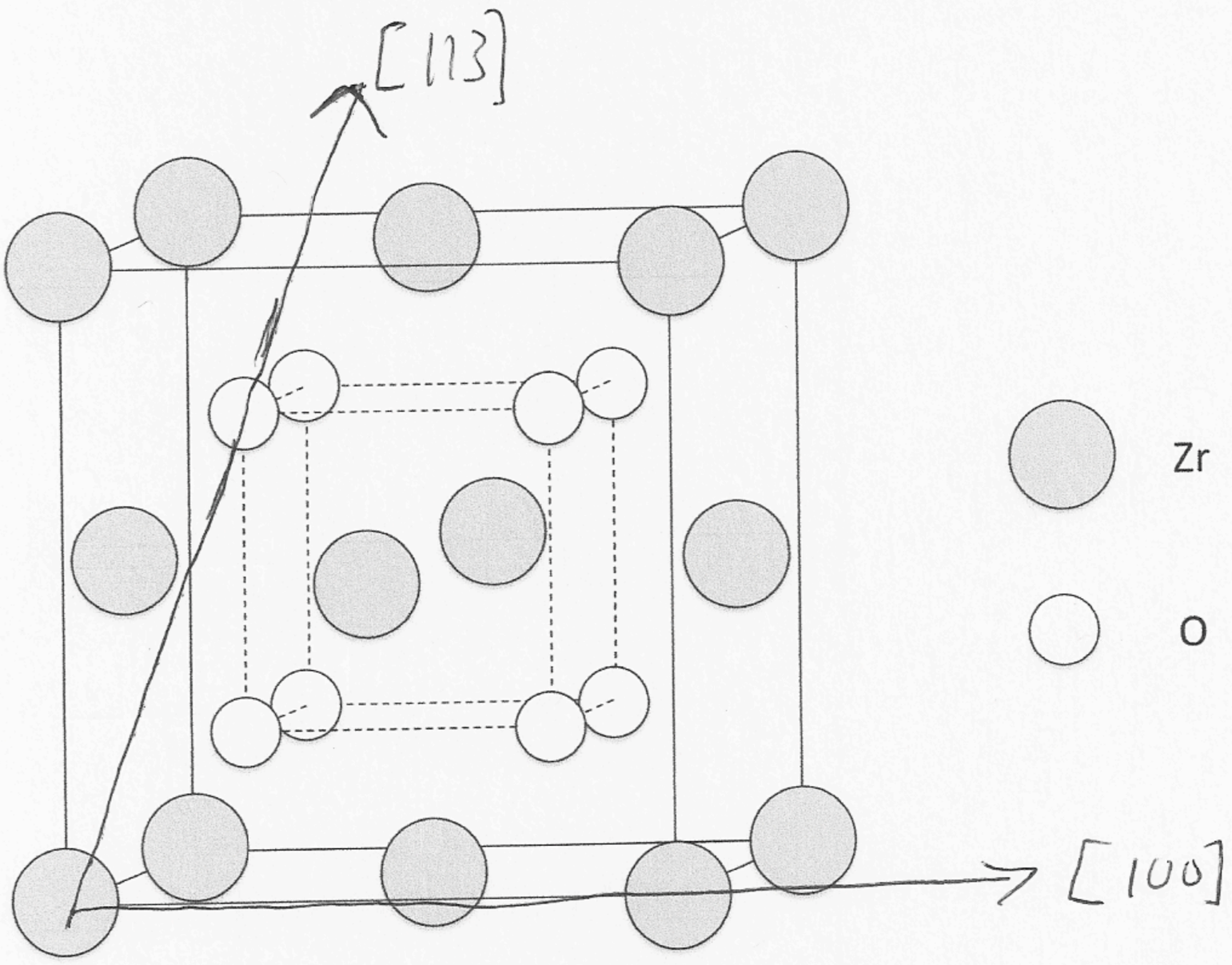
Consider diagonal of cube:

$\sqrt{3} \cdot 2R = 2R + 2r$

where r is radius of impurity

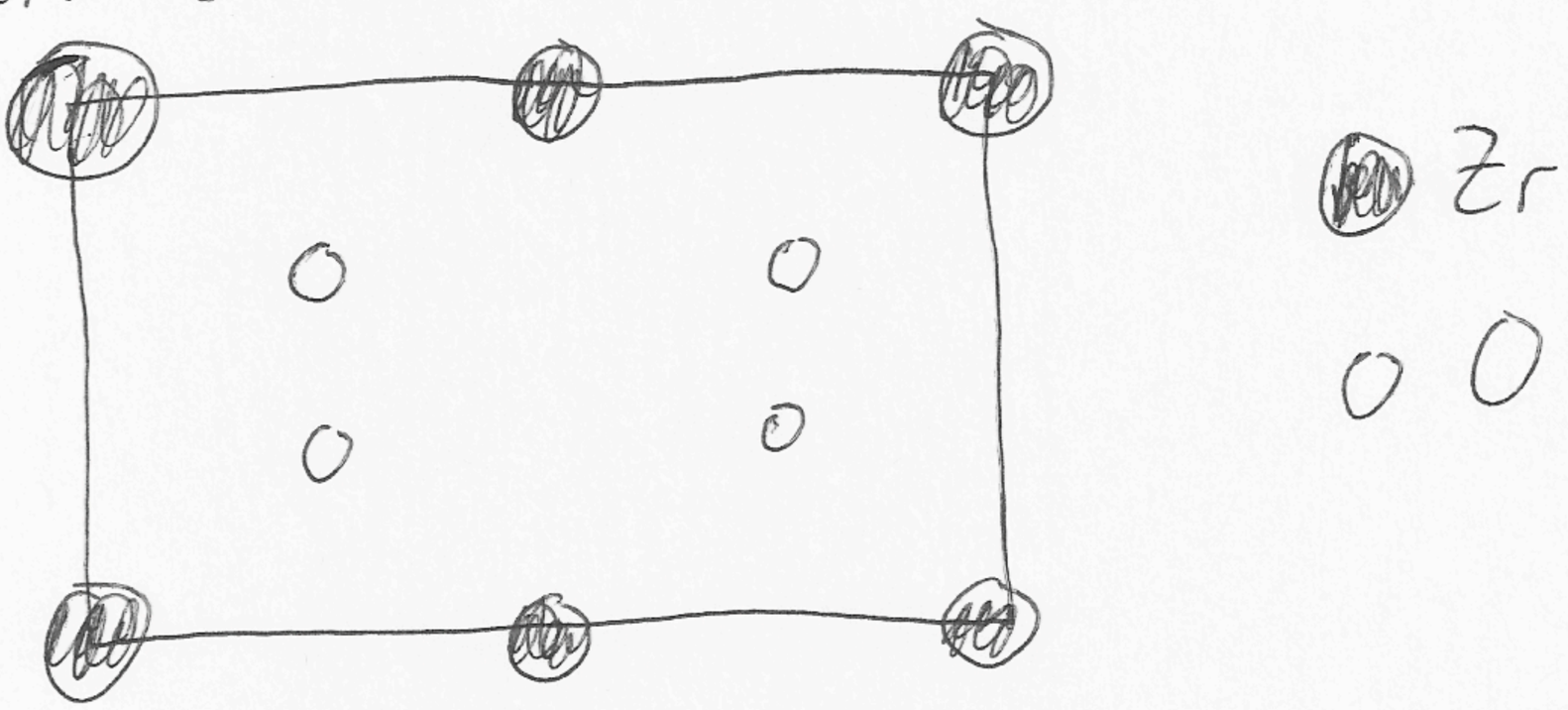
$(\sqrt{3} - 1)R = r$

$\boxed{r = 1.01\,\text{Å}}$



Crystal structure or ZrO_2. Use this figure in answering Problem 1.

For Problem 1b:



Problem 2: Defects.

(a) (10 points) For the ZrO_2 crystal structure considered in the previous problem, what type of vacancy (anion or cation) might form when an Al^{3+} ion is added as an impurity? What is the number of vacancies that will be formed per Al impurity?

anion Vacancy = oxygen Vacancy

one oxygen Vacancy per two Al impurities

since each oxygen Vacancy gives 2 missing negative charges and each Al^{3+} gives one missing positive charge

(b) (10 points) A researcher reports observing a screw dislocation in a bcc crystal with a line direction of [112]. Given that the Burger's vector must be one of the vectors connecting nearest-neighbor atoms in a bcc crystal, do you believe the researcher's claim? Explain.

$\vec{b}$ must be one of 8 nearest-neighbor vectors:

$[\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}]$ $[\frac{1}{2}\ \frac{1}{2}\ \bar{\frac{1}{2}}]$ $[\frac{1}{2}\ \bar{\frac{1}{2}}\ \frac{1}{2}]$ $[\bar{\frac{1}{2}}\ \frac{1}{2}\ \frac{1}{2}]$

$[\bar{\frac{1}{2}}\ \bar{\frac{1}{2}}\ \bar{\frac{1}{2}}]$ $[\frac{1}{2}\ \frac{1}{2}\ \bar{\frac{1}{2}}]$ $[\bar{\frac{1}{2}}\ \frac{1}{2}\ \bar{\frac{1}{2}}]$ $[\bar{\frac{1}{2}}\ \bar{\frac{1}{2}}\ \frac{1}{2}]$

None of these vectors is parallel to $\vec{L} = [112]$

so this cannot be screw

(c) (15 points) For an elemental metal the number density of vacancies (N_v) and the number density of lattice sites (N) is measured at different temperatures as follows:

Temperature (K)	300	400	500
N (m^{-3})	6.0214×10^{28}		5.9419×10^{28}
N_v (m^{-3})	1.0476×10^{17}	9.0613×10^{19}	5.227×10^{21}

What is the vacancy formation energy (Q) and the value of N at temperature $T = 400$ K?

$T_1 = 300\ k \quad T_2 = 400\ k \quad T_3 = 500\ k$

$$\frac{N_V(T_1)}{N_V(T_3)} = \frac{N(T_1)}{N(T_3)} \exp\left[-\frac{Q}{k}\left(\frac{1}{T_1} - \frac{1}{T_3}\right)\right]$$

$$\ln\left[\frac{N_V(T_1)\,N(T_3)}{N(T_3)\,N_V(T_1)}\right] = -\frac{Q}{k}\left(\frac{1}{T_1} - \frac{1}{T_3}\right)$$

$$\Rightarrow \boxed{Q = 0.7\ eV}$$

$$N(T_2) = N_V(T_2) \exp\left[\frac{Q}{kT_2}\right]$$

$$\boxed{N(T_2) = 5.9843 \cdot 10^{28}\ m^{-3}}$$

Problem 3: Polymers.

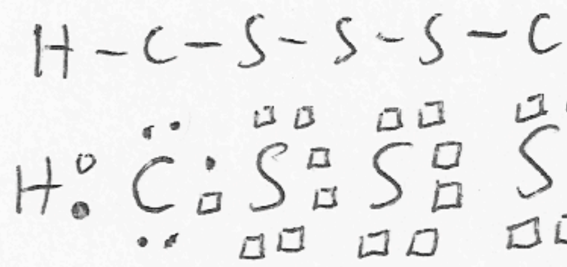
(a) (10 points) The figure below shows the atomic structure of neighboring chains in a polymer material. Do you expect that this material is a thermoset or thermoplastic polymer? Explain.

Thermoset because the chains are cross-linked by S-S-S

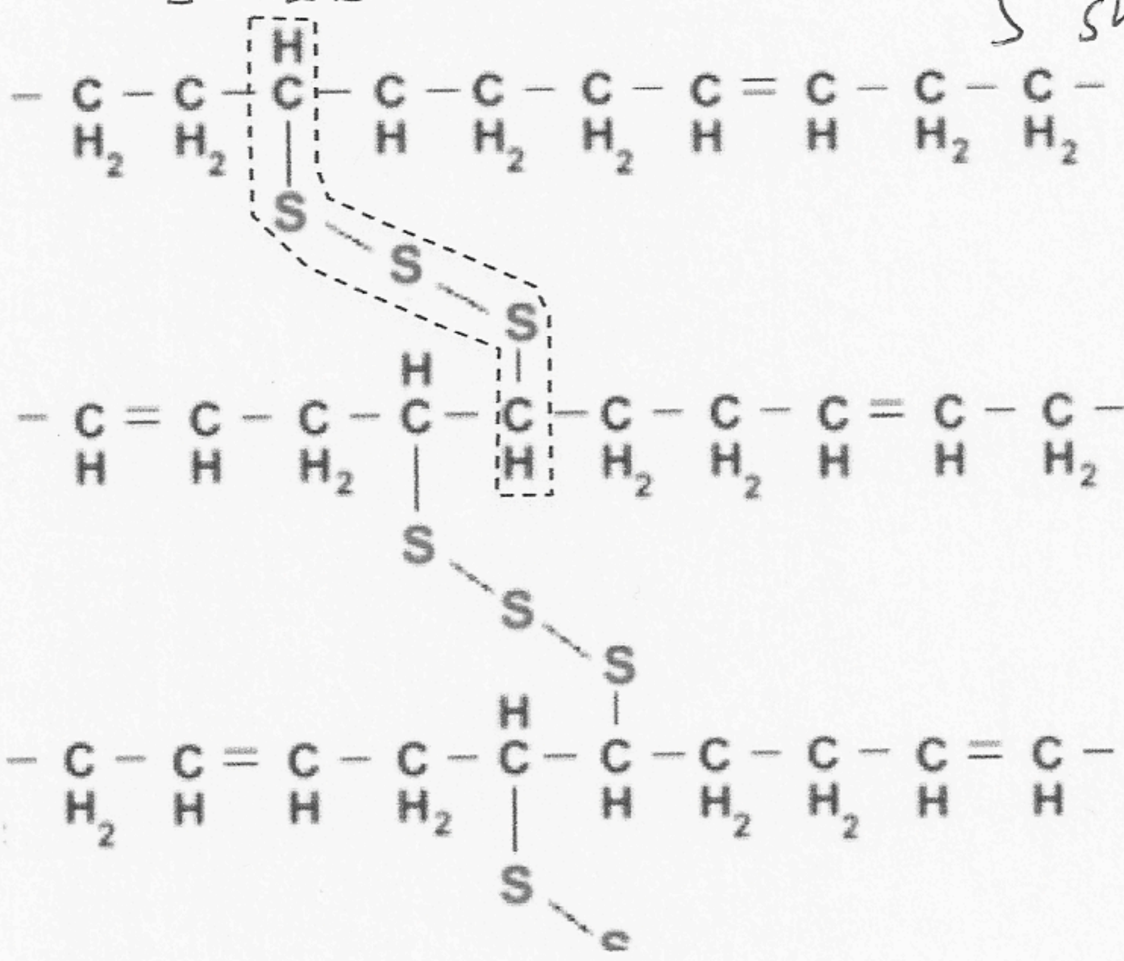
(b) (10 points) Argue, using Lewis-dot structures, that the bonds in the regions indicated with a dashed line are saturated covalent bonds.

H ⇒ 1 electron (denote by o)
C ⇒ 4 electrons (denote by •)
S ⇒ 6 electrons (denote by □)

H-C-S-S-S-C-H



H shares 2 electrons ✓
C shares 8 electrons ✓
S shares 8 electrons ✓



Structure of neighboring chains in a certain polymer material. The dashed lines surround a part of the molecule that is to be considered in part (b).