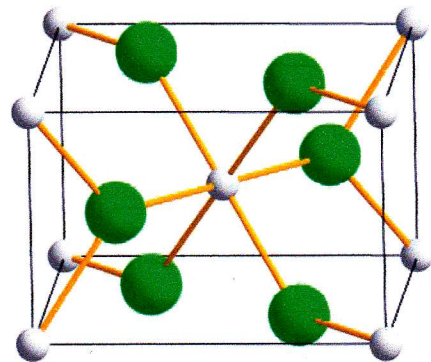
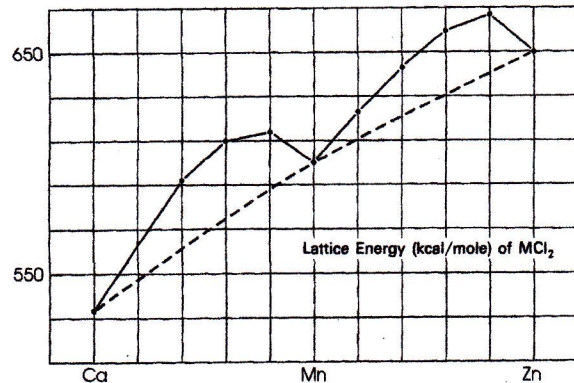


3. A plot of the lattice energies for  $MCl_2$  salts for  $M = Ca$  to  $Zn$  and a drawing of the unit cell are shown to the right. In the electrostatic model for “ionic bonding”  $U$  is proportional to  $(Z_+)(Z_-)e^2A/(r_+ + r_-)$  where  $Z_+$  and  $Z_-$  are the ion charges,  $A$  is the structure (Madelung) constant and  $r_+ + r_-$  are the radii of the ions (see p. 88 of the text for more on this). Since the radius of the cation should decrease systematically as the effective number charge increases on going across the fourth row, one might expect a similar smooth variation in the lattice energy. Clearly, this is not the case. Provide an explanation for the observed variation in lattice energy that accounts for the fact that the points for  $Ca^{2+}$ ,  $Mn^{2+}$  and  $Zn^{2+}$  define a nearly straight line that would appear to be consistent with the expected gradual decrease in their radii, whereas the other elements have somewhat greater lattice energies than predicted on this basis.



4. Use the experimentally determined values for  $\Delta_0$  for  $V^{2+}$  in solid  $VCl_2$  ( $9200\text{ cm}^{-1}$ ) and  $Ni^{2+}$  in solid  $NiCl_2$  ( $6920\text{ cm}^{-1}$ ) to support your explanation for the phenomena described in problem 3. This requires calculations of LFSE; example problem 20.3 will provide guidance for those who need help. Estimate the actual deviation in lattice energies from the predicted value based on the line connecting the values for  $Ca^{2+}$ ,  $Mn^{2+}$  and  $Zn^{2+}$  in the figure from problem 3.