

Spreadsheet Applications for Materials Science

The Ionic Bond

Introduction

A good place to start the study of engineering materials is with the nature of the energies and forces involved in the bonding between atoms. When we do we find that there are four principle types of bonds: ionic, metallic, covalent and Van der Waals. While bonding in most materials involves a combination of types of bonds it is still convenient to think of materials in terms of their dominant type of bonding. These generalizations are very useful since many fundamental properties are directly related to the nature and strength of these bonds. For example, ceramics and glasses, whose bonding is primarily ionic but may also have covalent traits, tend to be brittle, chemically inert, poor electrical and thermal conductors and may be optically transparent while metals, due to their primarily metallic bonding, are ductile, shiny and electrically and thermally conductive. Certain covalently bonded materials are among the hardest (diamond) and have the highest melting points. The chemical bonds in the best known semiconductors, silicon and germanium, are almost purely covalent. Clearly when we know something about a material's bonding we are in a better position to predict and even control its structure and properties. We can also make a number of generalizations regarding properties such as its melting point, stiffness and coefficient of thermal expansion even without having to consider the details of the band structure of inner and outer electron shells (the outer shells are most important in bonding and in the material's electrical properties). In fact, the methods of calculating these bonding energies and properties are, for the most part, quite simple.

The chemical bond consists of two parts, an attractive component which acts over relatively large distances and a repulsive component which dominates at small interatomic spacings. For purely ionic bonds the energy of attraction is primarily due to the coulombic attraction between the outer shells of the oppositely charged ions. The equation for the lattice energy of an ionic compound is given by

$$E_a = \frac{Mz_1z_2q^2}{4\pi\epsilon_0r} \quad (1)$$

where M is the Madelung constant, r is the interatomic spacing, ϵ_0 is the permittivity in free space, q is the elementary charge and z_1 and z_2 are the valences of two ions. The energy of repulsion is due to the overlapping of the negatively charged electric fields of the inner shells and the positively charged nuclei. While the exact expression for this energy is difficult to derive a good

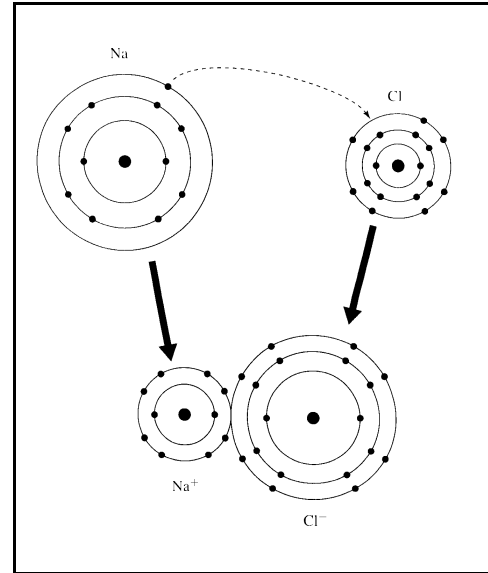


Figure 1. The formation of an ionic bond between a sodium and chlorine atom [1].

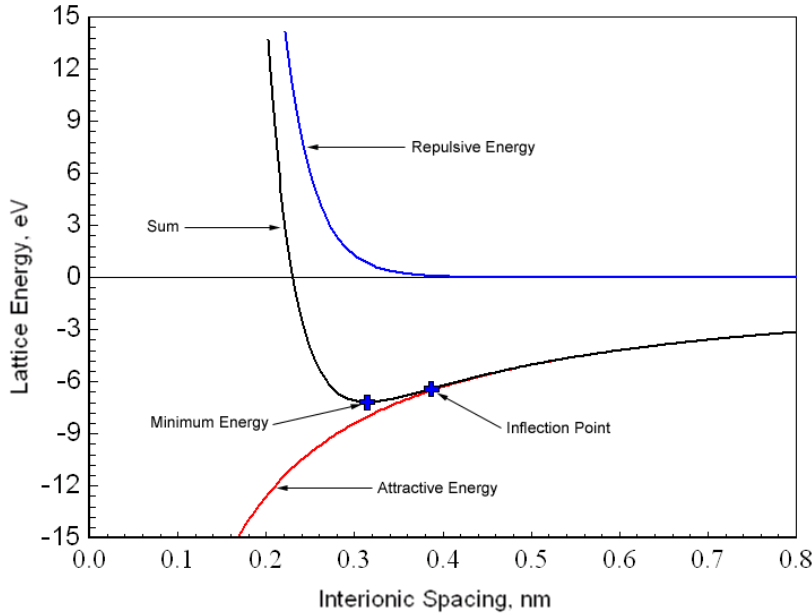


Figure 2 Calculated lattice energy for KCl.

approximation is given [2] by

$$E_r = b\lambda \exp\left(\frac{-r}{\rho}\right) \quad (2)$$

where b is the coordination number, λ is the repulsive energy coefficient and ρ is the repulsive range parameter. The total lattice energy is equal to the sum of the repulsive and attractive energies

Figure 2 shows the individual and combined lattice energies as a function of interatomic spacing. Note that at large spacings there is still a small energy of attraction which increases ever more rapidly as the atoms are brought closer together. On the other hand, the energy of repulsion is negligible at large spacings but when the atoms are brought close enough together this term increases very quickly and soon dominates. Adding these two curves produces a minimum in the total lattice energy curve which defines both the equilibrium energy and interatomic spacing. This minimum is given by the following equation:

$$E_0 = \frac{Mz_1z_2q^2}{4\pi\epsilon_0r_0} \left(1 - \frac{\rho}{r_0}\right) \quad (3)$$

where r_0 is the equilibrium spacing between nearest neighbors. A typical value for this equilibrium spacing is 0.3 nm and 6 eV is a typical value for this energy.

Mechanical (Elastic) Properties

The forces involved in the chemical bond are simply the first derivatives of bonding energies with respect to the interatomic spacing

$$F = \frac{dE}{dr} \approx \frac{\Delta E}{\Delta r} \quad (4)$$

By expressing chemical bonding in terms of forces we can better understand, and predict, certain mechanical properties, such as the elastic moduli, starting with the bulk modulus

$$K = \frac{1}{9r} \frac{1}{2} \frac{d^2E}{dr^2} \Big|_{r=r_0} = \frac{1}{9r} \frac{1}{2} \frac{dF}{dr} \Big|_{r=r_0} \approx \frac{1}{9r} \frac{1}{2} \frac{\Delta F}{\Delta r} \Big|_{r=r_0} \quad (5)$$

The bulk modulus describes the elastic behavior of a material subjected to hydrostatic pressures and is related to the mechanical force required to change the volume per atom. It is also related to the material's shear modulus, its resistance to elastic deformation by shear forces, by the equation

$$G = \frac{3K(1-2\nu)}{2(1+2\nu)} \quad (6)$$

and to Young's modulus, the material's stiffness in uniaxial tension and compression, by

$$Y = \frac{3K(1+\nu)(1-2\nu)}{(1+2\nu)} \quad (7)$$

where ν is Poisson's ratio. The value of Poisson's ratio ranges from 0.1 for ceramics to 0.3 for metals.

Thermal Properties

Calculations of bond energies and spacing and the corresponding experiments are often done for temperatures at absolute zero, although they are also done for other temperatures. When we examine the results for the different temperatures we find that as the temperature increases the magnitude of the bond energy decreases and the equilibrium spacing between ions increases. This increase in spacing is what is commonly called thermal expansion and is one manifestation of the energy required to change the volume per atom. The decrease in the bond energy leads to an understanding of why materials become softer as they are heated. We also know from experience that if the temperature continues to increase the material will eventually reach a point where the bonds are so weak that atoms can easily move to other lattice sites, the crystalline structure may break down, and the material either melts or vaporizes. The amount of thermal energy required to melt the material is also shown in figure 2. Once we locate this point on the graph we should be able to estimate the melting point.

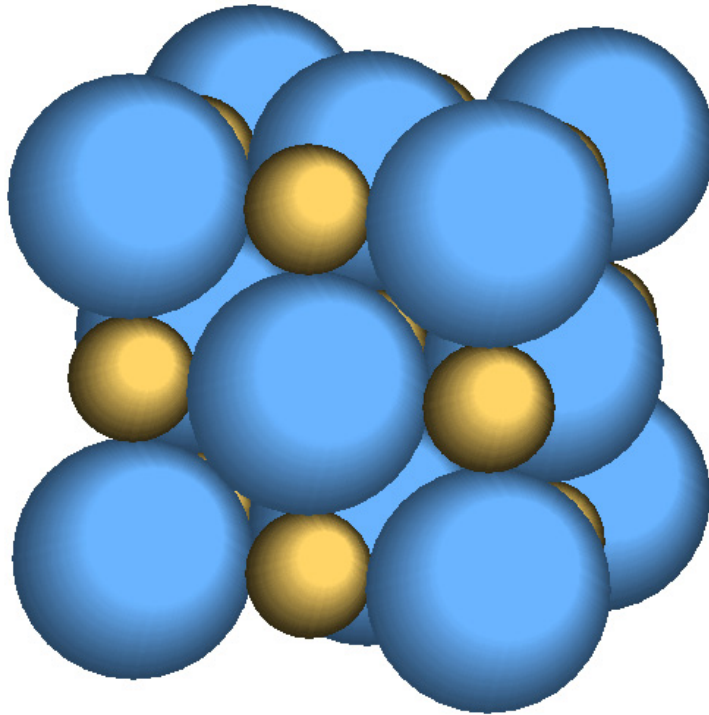


Figure 3. The NaCl-type structure is based on the fcc-unit cell with chlorine atoms at the lattice sites and sodium atoms at all octahedral sites. It could also be thought of as an fcc lattice with Na-Cl atoms pairs at each lattice site.

If the amount of thermal energy was greater than the lattice energy then the atoms in the structure would separate completely. Merely melting the material, however, would require considerably less thermal energy. The energy to cause melting is difficult to see in figure 2 but if we replot it as force versus distance then one will find a maximum slightly to the right of the equilibrium spacing. This is an interesting point which can be interpreted as the theoretical strength of the material, and the melting point.

The maximum on the $F-r$ curve corresponds to the inflection point on the $E-r$ curve. Once this energy E_l has been found one can then estimate the melting point of the material. The energy required to raise the temperature of the material to its melting point is given by

$$\frac{\Delta E}{n} = c\Delta T \approx 3k_B\Delta T \quad (8)$$

where c is the material's heat capacity, which can be approximated as $3k_B$ (k_B is Boltzmann's constant), and n is the number of lattice sites in the unit cell. The melting point can now be estimated using the following equation

$$T_{mp} \approx \frac{\Delta E}{n3k_B} + T_0 \quad (9)$$

where T_0 is the temperature for which E_0 was calculated. Note that in this approximation the contribution of entropy has been ignored.

References and Additional Resources

1. J.F.Shackelford, Introduction to Materials Science for Engineers, 4th edition, Prentice Hall, New Jersey, pp. 26-36, (1996).
2. C. Kittel, Introduction to Solid State Physics, 7th edition, John Wiley and Sons, New York, pp.66-73, (1996).
3. Handbook of Chemistry and Physics, R.Weast, ed., 65th edition, CRC Press, Inc, Boca Raton, FL, pp. F190-F191, (1984).
4. J.Shermon, Chemical Reviews, vol. 11, pp.93-170, (1932).
5. H.H.Sisler, Electronic Structure, Properties and the Periodic Law, 2nd edition, D.Van Nostrand, New York, pp.65-69, (1973).
6. G.Simmons and H.Wang, Single Crystal Elastic Constants and Calculated Aggregate Properties, A Handbook, 2nd edition, The M.I.T. Press, Cambridge Massachusetts, (1971).
7. O.H.Wyatt and D.Dew-Hughes, Metals, Ceramics and Polymers, Cambridge University Press, pp.67-69, (1974).
8. L.Pauling, The Nature of the Chemical Bond, 3rd edition, Cornell University Press, Ithaca, NY, pp. 505-510, (1960).
9. C.Giacovazzo, H.L.Monaco, D.Viterbo, F.Scordari, G.Gilli, G.Zanotti, M.Catti, Fundamentals of Crystallography, International Union of Crystallography, Oxford University Press, pp.410-413, (1992).
10. ICDD Powder Diffraction Database, Sets 1-46, (1997).

Ionic Bonding Spreadsheet Project

In this project you will build a computer model of ionic bonding that will allow you to model any of the compounds listed in table 2 and, with minor revisions, practically any ionic compound. The procedure has two steps:

1. Build the model and verify that it works for KCl.
2. Use your validated model to investigate other compounds listed in table 2.

Start building your spreadsheet by defining all terms, parameters and constants that are used in these equations and make sure the units of measure for each are consistent. Next, define the parameters for the particular material whose bonding behavior is being modeled. After this it will be possible to compute the attractive, repulsive and total bond energies and then, taking the first derivative to be the central difference of these energy-distance data, one can compute the force-distance curves. When this is done one will be able to extract several physical properties, specifically:

Interatomic Spacing	Locating the minimum in the energy-distance data one can determine the interatomic (interatomic) spacing.
Bond Strength	The minimum on the energy-distance curve gives the strength of the bonds in the lattice.
Elastic Moduli	The bulk modulus (compressibility) can be computed using equation 8. Provide your own estimate of Poisson's ratio and compute the tensile and shear moduli.
Melting point	Compute the energy required to reach melting point but not complete the melting process. Do this using a rough approximation of heat capacity.
Density	Calculate the density of your material from the mass and volume of a single unit cell.

The spreadsheet printout at the end of this document (before the appendix) shows the results for modeling of KCl. Compare these to your results. The agreement should be perfect. Even small differences in the third digit to the right of the decimal point hint at errors such as truncating the values of the conversion factors and physical constants.

After validating your model for the case of KCl repeat them for other materials listed in table 2.

Note – Consider the value of Poisson's ratio listed in table 2 to be nominal and that adjusting it $\pm 10\%$ in your modeling would be acceptable.

Note – Bonding in the lithium compounds have a significant covalent component.

Helpful Constants, Conversion Factors, and Equations

Physical Constants

Avogadro's Number	N_A	$6.022045 \times 10^{23} \text{ mol}^{-1}$
Boltzmann's Constant	k_B	$1.380662 \times 10^{-23} \text{ J K}^{-1}$
Elementary Charge	q	$1.6021892 \times 10^{-19} \text{ C}$
Permittivity of Free Space	ϵ_0	$8.85418782 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2} \text{ or } \text{C}^2 \text{ J}^{-1} \text{ m}^{-1}$

Conversion Factors

1 eV	$1.6021917 \times 10^{-19} \text{ J}$
1 MPa	145 psi
1 calorie	4.184 J

Distance Between Any Two Points

The following equation gives the distance between point 1 and point 2 where their coordinates x, y, z are defined for any of the seven crystal systems where a, b and c and α, β and γ have their usual meanings.

$$d_{12}^2 = (x_1 - x_2)^2 a^2 + (y_1 - y_2)^2 b^2 + (z_1 - z_2)^2 c^2 + 2(x_1 - x_2)(y_1 - y_2) ab \cos \gamma + \quad (10)$$
$$2(y_1 - y_2)(z_1 - z_2) bc \cos \alpha + 2(z_1 - z_2)(x_1 - x_2) ca \cos \beta$$

Note that for orthogonal structures the cosine terms drop out.

Table 1. Crystallographic data for selected compounds [2,3,4,10]

Substance	Mineral Name	Crystal Lattice	Lattice Constants, nm	Madelung Constant	Density, Mg/m ³	PDF File Number
KBr	-	FCC (NaCl-type)	a=0.660050	1.747565	2.749	36-1471
KCl	Sylvite	FCC (NaCl-type)	a=0.629170	1.747565	1.988	41-1476
KF	Carobbiite	FCC (NaCl-type)	a=0.534758	1.747565	2.523	36-1458
KI	-	FCC (NaCl-type)	a=0.706550	1.747565	3.126	04-0471
LiBr	-	FCC (NaCl-type)	a=0.550130	1.747565	3.465	06-0319
LiCl	-	FCC (NaCl-type)	a=0.513960	1.747565	2.074	04-0664
LiF	Griceite	FCC (NaCl-type)	a=0.402700	1.747565	2.638	04-0857
LiI	-	FCC (NaCl-type)	a=0.600000	1.747565	4.116	01-0592
NaBr	-	FCC (NaCl-type)	a=0.597353	1.747565	3.206	36-1456
NaCl	Halite	FCC (NaCl-type)	a=0.564020	1.747565	2.163	05-0628
NaF	Villiumite	FCC (NaCl-type)	a=0.463329	1.747565	2.804	36-1455
NaI	-	FCC (NaCl-type)	a=0.647300	1.747565	3.671	06-0302
RbBr	-	FCC (NaCl-type)	a=0.688900	1.747565	3.360	08-0480
RbCl	-	FCC (NaCl-type)	a=0.658100	1.747565	2.818	06-0289
RbF	-	FCC (NaCl-type)	a=0.565160	1.747565	3.844	22-0886
RbI	-	FCC (NaCl-type)	a=0.734200	1.747565	3.564	06-0218
TiO ₂	Rutile	Tetragonal	a=0.45933, c=0.29592	2.248037	4.250	21-1276
TiO ₂	Anatase	Tetragonal	a=0.37852, c=0.95139	2.400000	3.893	21-1272
ZnS	Sphalrelite (Zinc Blend)	FCC	a=0.54060	1.638060	4.097	05-0566
ZnS	Wurtzite	Hexagonal	a=0.382098, c=0.62573	1.641320	4.090	36-1450
SiO ₂	β-Quartz	Hexagonal	a=0.511, c=0.537	4.1719	2.539	47-1144
CsCl	-	Cubic	a=0.41230	1.762670	3.989	05-0607
MgF ₂	Sellaite	Tetragonal	a=0.46200, c=0.30509	2.3810	3.177	41-1443
MgO	Periclase	NaCl-type	a=0.42112	1.747565	3.585	45-0946
ZnO	Zincite	Hexagonal	a=0.324982, c=0.520661	1.4985	5.675	36-1451
CdI ₂	-	Hexagonal	a=0.42481, c=1.37265	2.355	5.669	33-0239
Cu ₂ O	Cuprite	Cubic	a=0.42696	2.221240	6.106	05-0667
Al ₂ O ₃	Corundum	Rhombohedral	a=0.47587, c=1.29929	4.171900	3.987	46-1212
CaF ₂	Fluorite	Cubic	a=0.546305	2.3650	3.181	35-0816

Table 2. Selected room temperature properties of materials having the NaCl-type structure [2,3,6].

Substance	Interatomic Spacing nm	Repulsive Energy Parameter eV	Repulsive Range Parameter nm	Measured Lattice Energy eV	Calculated Lattice Energy eV	Gibb's Free Energy kJ/mol	Melting Point K	Bulk Modulus GPa	Poisson's Ratio	Shear Modulus GPa	Young's Modulus GPa
KBr	0.3298	2392.6	0.0336	-6.886	-6.908	-380.8	1007	15.1	0.254	8.9	22.2
KCl	0.314655	2132.5	0.0326	-7.190	-7.008	-409.2	1043	17.4	0.249	10.5	26.2
KF	0.2674	1362.7	0.0298	-8.230	-8.200	-537.8	1131	31.1	0.260	17.8	44.9
KI	0.3533	2964.7	0.0348	-6.500	-6.266	-324.9	954	11.7	0.251	7.0	17.5
LiBr	0.2751	614.8	0.0340	-8.230	-7.849	-342.0	823	25.7	0.248	15.6	38.9
LiCl	0.2570	509.7	0.0330	-8.621	-8.365	-384.4	878	31.8	0.238	20.2	50.0
LiF	0.2014	307.9	0.0291	-10.507	-10.503	-587.7	1118	66.6	0.198	50.5	120.9
LiI	0.3000	623.1	0.0366	-7.706	-7.203	-270.2	722	17.1	0.200	10.99	26.38
NaBr	0.2989	1383.5	0.0328	-7.528	-7.337	-348.9	1020	19.9	0.250	11.9	29.8
NaCl	0.282010	1092.3	0.0321	-7.918	-7.745	-384.2	1074	23.9	0.249	14.4	36.0
NaF	0.231710	666.8	0.0290	-9.297	-9.332	-543.5	1266	48.1	0.231	31.6	77.7
NaI	0.3237	1643.6	0.0345	-7.077	-6.791	-286.1	934	16.1	0.274	8.6	21.9
RbBr	0.3445	3151.9	0.0338	-6.617	-6.431	-381.8	966	13.8	0.268	7.6	19.2
RbCl	0.3291	3318.4	0.0323	-6.908	-6.739	-407.8	991	16.2	0.268	8.9	22.6
RbF	0.2815	1851.6	0.0301	-7.866	-7.823	-	1068	27.3	0.276	14.4	36.9
RbI	0.3671	4150.6	0.0348	-6.283	-6.054	-328.9	920	10.8	0.262	6.1	15.5
MgO	0.2110	-	-	-	-42.405	-569.4	2852	153.3	0.172	128.6	301.5
CaO	0.2100	-	-	-	-37.437	-604.0	2614	-	-	-	-

File: Ionic Bonding-2.xls
 Owner: Mike Meier
 Created: June 19, 1997
 Revised: January 11, 2003
 Description: Calculation of ionic bonding energies, forces and related properties for materials with the NaCl-type structure.

Conversion Factors

From	To	Value	Units
Joules	eV	6.242E+18	eV/J
Coulombs	eV s	6.242E+18	eV s/C
GPa	ksi	145	ksi/GPa
Calories	Joules	4.184	J/cal

Physical Constants

Avogadro's Number:	6.022E+23	per mole	
Boltzmann's Constant:	1.381E-23	J/K	8.618E-05 eV/K
Proton Charge:	1.602E-19	C	
Velocity of Light:	2.998E+08	m/s	
Permittivity:	8.854E-12	C ² /Nm ²	

Environmental Parameters

Temperature:	298	K
Pressure:	1	atmospheres

Material

Substance:	KCl			
Mineral Name:	Sylvite			
Melting Point:	1043	K		
Density:	1.988	Mg/cm ³		
Crystal Lattice:	NaCl type			
Lattice Constants:	0.629170	0.629170	0.629170	a,b,c in nm
Lattice Angles:	90.000	90.000	90.000	degrees
Equivalent Sites:	4			
Coordination Number:	6			
Reference Ion:	0	0	0	u,v,w
Nearest Ion:	0	0	0.5	u,v,w
	Type	Number	Valence	At.Wt.
Cation:	K+	4	1	39.0983
Anion:	Cl-	4	-1	35.453

Interionic Spacing (independent variable)

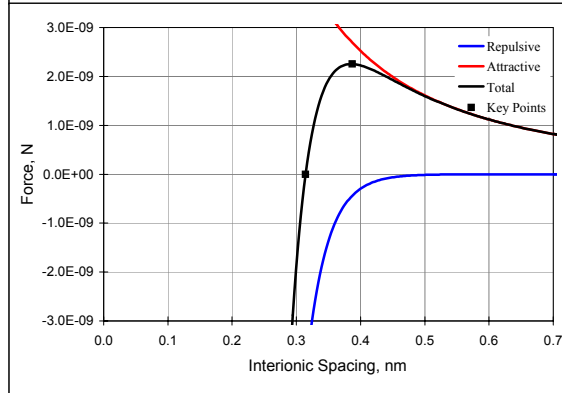
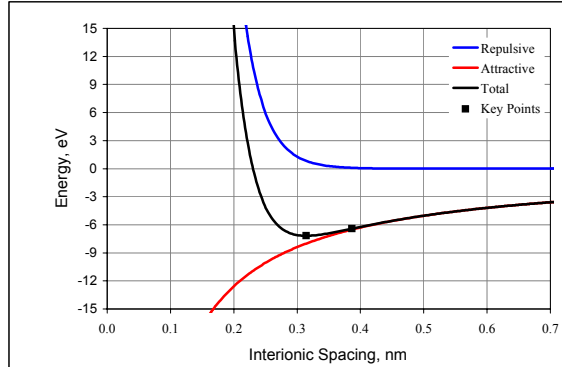
Initial Value:	0.061895	nm
Increment:	0.002500	nm

Repulsive Energy

Energy Parameter:	2132.5	eV
Range Parameter:	0.032600	nm

Coulombic Attraction

Madelung Constant: 1.747565



Results

Property	Reference	Calculated	Units	Calculated	Units	Difference	Note
Cell Containing E min:	-	-	-	-	-	-	Uses the Quattro Pro @MinLookup function on column D
Cell Containing F max:	-	-	-	-	-	-	Uses the Quattro Pro @MaxLookup function on column G
Equilibrium Spacing:	0.314585	0.314395	nm	3.14395	Angstroms	-0.06%	Ionic spacing at the minimum for column D
Lattice Constant, a:	0.629170	0.628790	nm	6.28790	Angstroms	-0.06%	For this structure, a=2r0
Energy Minimum:	-7.190	-7.176	eV	-692.3	kJ/mole	-0.20%	Minimum, column D
Total Lattice Energy:	-7.190	-7.175	eV	-692.2	kJ/mole	-0.21%	Equation 4
Force at Emin:	n/a	#VALUE!	N	-	-	-	Minimum, column G, absolute value
dF/dr at F=0:	n/a	99.299	N/m	-	-	-	dF/dr at E min
Bulk Modulus:	17.40	17.55	GPa	2.54	1e6 psi	0.84%	Equation 6
Poisson's Ratio:	0.249	0.215	-	-	-	-	t the correct value for the shear modulus.)
Shear Modulus:	10.50	10.49	GPa	1.52	1e6 psi	-0.08%	Equation 7
Young's Modulus:	26.20	25.49	GPa	3.70	1e6 psi	-2.70%	Equation 8
Maximum Force:	n/a	2.252E-09	N	-	-	-	Maximum, column G
Energy at F max:	n/a	-6.415	eV	-	-	-	Energy at maximum for column G
delta E:	n/a	0.760	eV	73.4	kJ/mole	-	-
Melting Point:	1043.0	1033.4	K	760.4	C	-0.92%	Equation 10
Mass:	n/a	4.952E-22	grams/u.cell	-	-	-	-
Density:	1.988	1.992	g/cm ³	-	-	0.19%	-

Ionic Spacing nm	Repulsive Energy eV	Attractive Energy eV	Total Energy eV	Repulsive Force Newtons	Attractive Force Newtons	Total Force Newtons	dF/dr N/m	Energy Data Symbols	Energy Data Labels	Force Data Symbols	Force Data Labels
0.061895	1916.374	-40.660	1875.714								
0.064395	1774.906	-39.082	1735.825	-8.731E-06	9.738E-08	-8.634E-06					
0.066895	1643.882	-37.621	1606.261	-8.086E-06	9.022E-08	-7.996E-06	2.456E+05				
0.069395	1522.530	-36.266	1486.264	-7.490E-06	8.383E-08	-7.406E-06	2.275E+05				
0.071895	1410.136	-35.005	1375.132	-6.937E-06	7.810E-08	-6.859E-06	2.108E+05				
0.074395	1306.039	-33.828	1272.211	-6.425E-06	7.293E-08	-6.352E-06	1.953E+05				
0.076895	1209.627	-32.729	1176.899	-5.950E-06	6.826E-08	-5.882E-06	1.809E+05				
0.079395	1120.332	-31.698	1088.634	-5.511E-06	6.402E-08	-5.447E-06	1.676E+05				
0.081895	1037.629	-30.730	1006.898	-5.104E-06	6.017E-08	-5.044E-06	1.553E+05				
0.084395	961.030	-29.820	931.210	-4.727E-06	5.666E-08	-4.671E-06	1.438E+05				
0.086895	890.087	-28.962	861.125	-4.378E-06	5.344E-08	-4.325E-06	1.332E+05				
0.089395	824.380	-28.152	796.228	-4.055E-06	5.049E-08	-4.005E-06	1.234E+05				
0.091895	763.524	-27.386	736.138	-3.756E-06	4.778E-08	-3.708E-06	1.143E+05				
0.094395	707.160	-26.661	680.499	-3.479E-06	4.528E-08	-3.433E-06	1.058E+05				
0.096895	654.958	-25.973	628.984	-3.222E-06	4.297E-08	-3.179E-06	9.804E+04				
0.099395	606.608	-25.320	581.289	-2.984E-06	4.084E-08	-2.943E-06	9.080E+04				
0.101895	561.828	-24.699	537.130	-2.764E-06	3.886E-08	-2.725E-06	8.410E+04				
0.104395	520.354	-24.107	496.247	-2.560E-06	3.702E-08	-2.523E-06	7.788E+04				
0.106895	481.941	-23.543	458.398	-2.371E-06	3.530E-08	-2.335E-06	7.213E+04				
0.109395	446.364	-23.005	423.359	-2.196E-06	3.371E-08	-2.162E-06	6.680E+04				
0.111895	413.413	-22.491	390.922	-2.034E-06	3.222E-08	-2.001E-06	6.187E+04				
0.114395	382.895	-22.000	360.895	-1.884E-06	3.082E-08	-1.853E-06	5.729E+04				
0.116895	354.629	-21.529	333.100	-1.744E-06	2.952E-08	-1.715E-06	5.306E+04				
0.119395	328.451	-21.078	307.372	-1.616E-06	2.830E-08	-1.587E-06	4.913E+04				
0.121895	304.204	-20.646	283.558	-1.496E-06	2.715E-08	-1.469E-06	4.550E+04				