

5. Concluding remarks

The systematic application of integral-equation theory has permitted straight-forward derivations of analytical expressions for the field generated by two coupled waves. Furthermore, the method has the advantage of being easily accessible to a physical interpretation. When an X-ray wave is transmitted over a small distance inside a crystal the probability for a single scattering event is much higher than the probability for double scattering, triple scattering and so on. The basis for the utility of the numerical method (40) is therefore that the successive layers in the crystal are chosen so close together that the probability for multiple reflection can be neglected. Since being over s_h and s_0 , however, the two integrals must be proportional to the probability for scattering and re-scattering, respectively. This must mean that a general

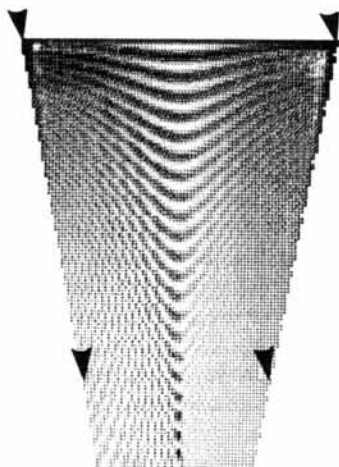


Fig. 6. The intensity of the transmitted wave as calculated from the numerical solution (40) of two coupled integral equations for the field. Fanning planes, not shown, converge above the crystal with $R = 20$ m. The arrows point in the direction of the incoming plane wave. (See text.)

term of n th order in any of the analytical iteration procedures has to be identical with the contribution from waves that are scattered and re-scattered n times. So far, the influence of average absorption, asymmetrical reflections, and coupling of three or more waves has been neglected. In many circumstances, for instance spectrometry, these factors are either trivial or unimportant. Complicated phenomena such as, for instance, diffraction focusing require that effects due to crystal shape and refraction are considered for the various classes of incoming wave packets.

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The Theory of the Pauling–Simon Law on Lattice Constants of Close-Packed Ordered Alloys

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Abstract

In close-packed ordered alloys of composition AB_n , the lattice constant a and all interatomic distances are determined to a good approximation by the quantity $(R_A + nR_B)$. This observation, the Pauling–Simon law [Pauling (1957). *Acta Cryst.* **10**, 374–375; Simon

(1983). *Angew. Chem.* **22**, 95–113], is analogous to Vegard's law [Pearson (1972). *The Chemistry and Physics of Metals and Alloys*. New York: Wiley] for random alloys. No exact proof is possible but here a theoretical discussion is given using the spirit of Froyen & Herring's 'proof' of Vegard's law [Froyen & Herring (1981). *J. Appl. Phys.* **52**, 7165–7167]. The

effect of a change in radius ratio can be discussed precisely with the virial $\sum_i F_i D_i$ either in terms of the exact crystal structure surrounding each type of atom or by approximating it as a close-packed medium treated as a uniform isotropic continuum. The essential point is that the *A* and *B* sites have to be elastically equivalent in the sense that a radius change δR on either site has to produce the same overall volume change. From this it is found that the interatomic force constant is proportional to D^{-m} , where *D* is the spacing between atoms and *m* lies between 3 and 4, more or less consistent with Badger's law [Badger (1934). *J. Chem. Phys.* **2**, 128–131].

1. Significance of the Pauling–Simon law

It is well known that the lattice constants *a* and interatomic distances *D* in solids are given by adding up appropriately defined atomic radii (Pauling, 1957; Simon, 1983). For solid-solution alloys $A_{1-c}B_c$ of concentration *c*, one has the well-known Vegard's distance law (Pearson, 1972) that *a* and hence the average *D* depends only on the average

$$R_{av} = (1 - c)R_A + cR_B, \quad (1.1)$$

where R_A and R_B are the atomic radii. This is not the place to discuss precisely how accurately it is or is not obeyed in particular systems. Suffice it to note that it is a sufficiently good or interesting approximation for the law to be universally known.

Froyen & Herring (1981) have discussed under what approximation, for what model of atoms and their forces, Vegard's law can be proved to be true. Their approach is to replace all atoms by average atoms with radius R_{av} giving a lattice constant

$$a = CR_{av}, \quad (1.2)$$

where *C* is a constant, and to consider the response of the system to changing any one atom from radius R_{av} to either R_A or R_B , *i.e.* introducing an appropriate δR . Since in solid solution all sites are equivalent, the δa resulting from a δR on any site is the same, *i.e.*

$$\delta a = (C/N)\delta R, \quad (1.3)$$

where *N* is the number of sites. To go from the system of average atoms to the real system, we have to introduce a change

$$\delta R^{(A)} = R_A - R_{av} \quad (1.4)$$

on $N(1 - c)$ sites and a change

$$\delta R^{(B)} = R_B - R_{av} \quad (1.5)$$

on Nc sites. As we are considering a linear response to the changes δR the total change in lattice constant is given by

$$\delta a = C[(1 - c)\delta R^{(A)} + c\delta R^{(B)}]. \quad (1.6)$$

This is zero by the definition of R_{av} . Hence, changing

from the system of average atoms to the real system produces no change in the lattice constant and so *a* for the real system is given by (1.2) in terms of the weighted average R_{av} . This is Vegard's law. The crucial point is that a δR on *any site* produces the *same* δa because all the sites are equivalent in the simple solid-solution case. This is evident from (1.6) in that the same constant *C* applies to both parts of the equation.

For the case of stoichiometric ordered alloys AB_n , the Pauling–Simon result also holds in spite of the fact that the *A* and *B* atoms occupy quite different sites in general. The lattice constant is again determined by a weighted average radius (Simon, 1983) so that

$$a = \frac{C}{n+1}(R_A + nR_B). \quad (1.7)$$

We restrict our discussion to the case where all atoms are on special sites so that all interatomic distances are determined by a single lattice constant *a*. We consider the cubic Laves phase ($MgCu_2$) and the CaF_2 structures, and orderings on a basic b.c.c. or f.c.c. lattice, *e.g.* CsCl, NaTl, NaCl and $AuCu_3$ structures. Indeed, for the latter compounds the Froyen–Herring argument applies directly as all sites in the b.c.c. and f.c.c. structures are equivalent, which proves the Pauling–Simon result in those cases. This is not true for the CaF_2 structure or the Laves phase where we are dealing with geometrically inequivalent sites. In the cubic Laves phase, for example, one site has 12 neighbours while the other has 16. However, it is clear from the argument leading from (1.2) to (1.6) that the Pauling–Simon result will still follow if the sites are in some sense *elastically equivalent*.

We can rephrase the argument (1.2) to (1.6) for the stoichiometric AB_n case by starting with an ideal system which now consists of atoms with some radius ratio R_A/R_B , which is ideal for the particular structure. We again consider the change in lattice constant due to a change δR_A on a single *A* site or δR_B on one *B* site:

$$\delta a = C_A \delta R_A / N(n+1) \quad \text{or} \quad \delta a = C_B \delta R_B / N(n+1). \quad (1.8)$$

This is for a specimen containing *N* formula units of AB_n so that there are $N(n+1)$ atoms altogether. If we make a change δR_A on all *N* atomic *A* sites and a change δR_B on all Nn *B* sites linearity implies that we obtain a change in lattice constant of

$$\delta a = \frac{1}{n+1}(C_A \delta R_A + nC_B \delta R_B). \quad (1.9)$$

This equation can be integrated to yield

$$a = \frac{1}{n+1}(C_A R_A + nC_B R_B), \quad (1.10)$$

where there is no extra constant term because a must shrink to zero if we shrink R_A and R_B uniformly to zero in the ideal ratio. Clearly if

$$C_A = C_B = C \quad (1.11)$$

then (1.10) becomes the Pauling–Simon law (1.7). Equation (1.11) is what we mean by saying that the A and B sites are ‘elastically equivalent’. We see that this condition suffices to give the Pauling–Simon result, and our analysis in §§ 2 and 3 will focus on it and on the type of force law required to satisfy it.

In order to bring out the significance of the Pauling–Simon result it is useful to consider Pearson near-neighbour diagrams (Pearson, 1972) which we will use to illustrate three points. Such a diagram is a plot of the structural strain parameter S versus radius ratio, where

$$S = (2R_A - D_{AA})/2R_B \quad (1.12)$$

is the difference between the actual interatomic distance D_{AA} and the distance $2R_A$ for a simple strain-free AA contact. Clearly the horizontal line $S=0$ in Fig. 1 is the line for strain-free AA contacts, the area below the line corresponds to a compressed contact and that above to a loose contact. The two lines representing strain-free AB and BB contacts are also plotted: they follow from simple geometry. In general, the positions of such lines depend on structural variables such as c/a or internal position parameters, but we have chosen the cubic Laves phases for analysis because there are no free parameters and the strain-free lines are uniquely determined.

For the sake of definiteness we will discuss the cubic Laves phase (MgCu_2) but phrase our arguments quite generally. Although the Laves structure is usually described as close packed, there is no ratio R_A/R_B for which hard spheres can maintain all three contacts AA , AB and BB exactly. For absolutely incompressible spheres we would expect that the observed strain parameters for different alloys would follow the kinked line $0VXY$ in Fig. 1 with different contacts dominating the structure as the radius ratio changes. In the absence of a unique radius ratio satisfying all three contacts, we will define an ideal ratio $(R_A/R_B)_{\text{ideal}}$ corresponding to the centroid of the triangle VWX in Fig. 1, or for simplicity what is nearly the same $(R_A/R_B)_{\text{ideal}} = (3/2)^{1/2} = 1.225$ corresponding to the point W . Alloys with radius ratio near this ideal value are observed to have strain parameters which lie roughly in the middle of the triangle VWX along the dashed line in Fig. 1. This means that the AB contacts are somewhat compressed while the AA and BB contacts are slightly expanded. From this we reach our first conclusion that the atoms are acting not quite as hard balls but as hardish, slightly deformable spheres where compression of one contact is being compensated by an expansion of another.

We next consider in more detail the argument leading to (1.10). On the assumption that the Laves alloys follow some systematic law, we suppose that the strain parameter S is some function of R_A/R_B represented by some curve in the Pearson diagram. For small deviations from the ideal radius ratio, such a curve can always be approximated by its tangent at the ideal ratio, *i.e.* by the line

$$S = \alpha[(R_A/R_B) - (R_A/R_B)_{\text{ideal}}] + \beta, \quad (1.13)$$

where α, β are constants. As the atoms are all on special sites we can express the interatomic distances D_{AA}, D_{BB} and D_{AB} as functions of the lattice constant, *i.e.*

$$D_{AA} = f_{AA}a, \quad D_{AB} = f_{AB}a, \quad D_{BB} = f_{BB}a, \quad (1.14)$$

where f_{AA}, f_{AB} and f_{BB} are geometrical constants. Using this in the definition of the strain parameter (1.12) and combining with the approximate straight line expression (1.13) we can express the lattice constant for R_A/R_B near the ideal ratio as

$$a = \mu(R_A + \gamma R_B) \quad (1.15)$$

where μ and γ are constants easily expressible in terms of α, β and $(R_A/R_B)_{\text{ideal}}$. Now experiment shows that all known alloys cluster quite well around a straight line (1.13) (Pearson, 1972; Simon, 1983), even for moderately large deviations of radius ratio from the ideal. This establishes that there is indeed an additivity of radii in the sense of (1.15), which is our second conclusion.

Equation (1.15) is clearly the same as (1.10), and the two independent constants μ, γ can be thought of as corresponding to two items of information. The first item is the fact that, for R_A/R_B equal to the ideal value, S in (1.13) is observed to have a value in the middle of the triangle VWX as already discussed.

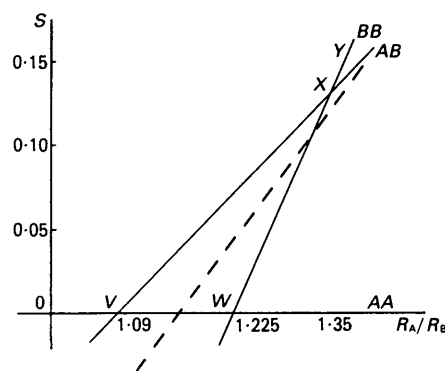


Fig. 1. Pearson near-neighbour diagram showing the strain parameter $S = (2R_A - D_{AA})/2R_B$ for the cubic Laves phase ($AB_n = \text{MgCu}_2$). The lines indicate strain-free contacts for the AA , AB , BB pairs of atoms, respectively. The experimental points for all alloys cluster around the dashed line (Simon, 1983; Pearson, 1972).

The second item of information is the slope of the dashed line representing data for non-ideal ratios (Figs. 1 and 2) and this is intimately connected with the Pauling–Simon law.

Comparison of (1.15) with (1.17) shows that the Pauling–Simon result requires $\gamma = n$. A little algebra from (1.12), (1.14) and (1.15) shows that the line (1.13) goes through the point

$$S = -\gamma \quad \text{for } R_A/R_B = -\gamma \quad (1.16)$$

as noted by Simon (1983), *i.e.* it cuts the 45° line $S = R_A/R_B$ at the point $(-\gamma, -\gamma)$. This is not of course a physical point, but it serves conveniently to define the slope of the line (1.13) of observed points in the Pearson diagram (Fig. 2). Simon has shown that the observed line is given remarkably well by the value $\gamma = n$. The data points, however, are all in the vicinity of the triangle VWX and it is clear from Fig. 2 that a small change in the slope of the dashed line through the points results in a large change in the value of γ . For the cubic Laves phase using Simon's data points we would estimate that γ could take values between 2 and 2.5. Our third point is therefore that the value $\gamma = n$ represents the observed data about as well as any other value. This is a graphical statement of the Pauling–Simon law and indeed is the form in which it was first noticed (Simon, private communication) and it applies to other cases besides the Laves phases (Simon, 1983).

This concludes the three deductions which we draw from the observed data and the Pearson near-neighbour diagram. To recap: (1) the observed data lies on a straight line implying that the lattice constant obeys an additivity of radii law; (2) the line passes through the centre of the triangle VWX which suggests that the atoms are acting as hardish yet deformable spheres; and (3) the slope of the line leads to the Pauling–Simon result.

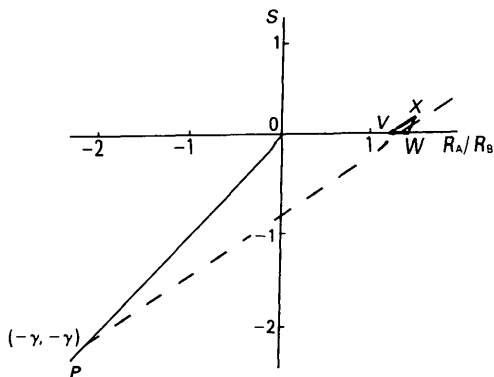


Fig. 2. Near-neighbour diagram for the cubic Laves phase on a smaller scale than in Fig. 1 showing the dashed line representing the real data points and its intersection with the 45° line OP .

2. Microscopic analysis of structures

We now consider the question of the type of force law that must exist between the atoms in order that the Pauling–Simon law is true. We assume a purely harmonic interaction with the potentials between the different pairs of atoms A and B given by

$$\begin{aligned} U_{AA}(D_{AA}) &= \lambda_{AA}(D_{AA} - 2R_A)^{1/2} \\ U_{AB}(D_{AB}) &= \lambda_{AB}(D_{AB} - R_A - R_B)^{1/2} \\ U_{BB}(D_{BB}) &= \lambda_{BB}(D_{BB} - 2R_B)^{1/2}. \end{aligned} \quad (2.1)$$

This will give a strain parameter in the near-neighbour triangle VWX (Fig. 1) with tight and loose contacts compensating each other. The equilibrium lattice spacing can be determined by minimizing the total energy. By writing the interatomic distances D in terms of the geometrical factors as in (1.14) and with a lattice constant of the form (1.15) we find that the value of γ in the equilibrium configuration is given by

$$\gamma = \frac{nN_{BB}\lambda_{BB}f_{BB} + N_{AB}\lambda_{AB}f_{AB}}{N_{AA}\lambda_{AA}f_{AA} + N_{AB}\lambda_{AB}f_{AB}}, \quad (2.2)$$

where N_{AA} , N_{AB} , N_{BB} are the numbers of near neighbours of each type AA , AB and BB (Table 1). We consider force constants λ which depend on the atomic sizes, *i.e.* on the interatomic spacings:

$$\begin{aligned} \lambda_{AA} &= \lambda_0(D_{AA})^{-m} = \lambda_0(f_{AA}a)^{-m} \\ \lambda_{AB} &= \lambda_0(D_{AB})^{-m} = \lambda_0(f_{AB}a)^{-m} \\ \lambda_{BB} &= \lambda_0(D_{BB})^{-m} = \lambda_0(f_{BB}a)^{-m} \end{aligned} \quad (2.3)$$

where λ_0 is some constant. It is natural that large atoms consist of less tightly bound electron shells and hence are softer. This is recognized in (2.3) by having $m > 0$ while $m = 0$ would make all force constants the same. There is no unique or natural argument about what m should be, and we will treat it as an adjustable parameter to see what value of m is consistent with the Pauling–Simon law, *i.e.* $\gamma = n$ in (2.2). In § 4 we return to what is known about interatomic forces, in particular Badger's rule, to compare with the value of m so found.

We can now apply this procedure to the cubic Laves phases (MgCu_2 structure) and the CaF_2 structure. We substitute (2.3) into (2.2) for different values of the exponent m and calculate γ (Table 2). The values of m which satisfy the Pauling–Simon law ($\gamma = n$) are 3.8 and 3.9 for the CaF_2 and MgCu_2 structures, respectively. For the compounds which are orderings on a simple f.c.c. or b.c.c. lattice where all sites are equivalent, it is easy to show from (2.2) that the Pauling–Simon law is true for all exponents m . It is worth mentioning at this point that the calculation is very dependent on which neighbours are included. The Laves phase and CaF_2 structures were chosen because the near neighbours are well defined. For

Table 1. *The geometrical factors f (1.14) and number of nearest neighbours N (in brackets) used for the calculation of γ (2.2)*

AB_n	f_{AA}	f_{BB}	f_{AB}
MgCu ₂	$\sqrt{3/4}$ (4)	$\sqrt{2/4}$ (6)	$\sqrt{11/8}$ (12)
CaF ₂	—	1/2 (6)	$\sqrt{3/4}$ (8)

Table 2. *Values of γ for the cubic Laves phase (MgCu₂) and CaF₂ structures (2.2) for different values of the exponent m*

m	MgCu ₂	CaF ₂
0	1.37	2.73
1	1.50	2.50
2	1.65	2.30
3	1.82	2.13
4	2.02	1.97
5	2.26	1.84

CaF₂, for example, we did not include the Ca–Ca neighbours [*i.e.* $N_{AA} = 0$ in (2.2)] as this interatomic distance is 40% greater than the F–F distance. For structures such as SiCr₃ the cut-off point is less obvious.

Alternatively, we can discuss the forces between atoms by considering the change in lattice constant caused by a change in the radius of some central atom. For the case of a linear response to the change in radius we have (Temkin, 1969)

$$\delta a = \frac{a}{9KN\Omega} \sum_i F_i D_i \quad (2.4)$$

where K is the bulk modulus, $N\Omega$ the total volume of the sample, F_i is the force at D_i due to a change in the radius of some central atom, and D_i is measured from the centre of the expanded atom to the centre of the neighbouring atoms i . This expression will serve to determine the desired constants C_A , C_B in (1.8) to (1.11). We now insert into (2.4) the forces from (2.1) and distances (1.14). For the expansion of a site- a atom by δR_A we therefore have a change in the lattice constant

$$\delta a = C_A \delta R_A / N(n+1) \quad (2.5)$$

as in (1.8), but we now have an expression for C_A :

$$C_A = \frac{(n+1)}{9K\Omega} (N_{AA} f_{AA} \lambda_{AA} + N_{AB} f_{AB} \lambda_{AB}). \quad (2.6)$$

A similar expression holds for the B sites. By noting that $nN_{BA} = N_{AB}$ we have

$$nC_B = \frac{(n+1)}{9K\Omega} (nN_{BB} f_{BB} \lambda_{BB} + N_{AB} f_{AB} \lambda_{AB}). \quad (2.7)$$

For the Pauling–Simon result to be true we require $C_A = C_B$ (1.11). Equating C_A and C_B in (2.6) and (2.7) leads to the same expression as (2.2) with $\gamma = n$.

Both approaches to the question of what force law operates between the atoms, *i.e.* minimizing the energy (2.1) and the use of the virial (2.4), give the same result. For CaF₂ and the cubic Laves phase the force constant must depend inversely on distance with an exponent $m \approx 3.8$ if the Pauling–Simon law is to be satisfied. We now consider a continuum approximation to try to understand why this should be so.

3. Continuum approximation for close packing

We will now repeat the procedure of the last half of § 2 but treating the surrounding medium as a uniform isotropic continuum instead of atomistically. We had the picture of some radius increase δR_A or δR_B on an atomic site pushing out the surrounding atoms and resulting in an overall change in lattice constant determined by the virial (2.4). We fitted the value of $m = 3.8$ – 3.9 in our force law (2.1) (2.3), by considering two specific structures and their detailed interatomic distances. However, all these alloys are close-packed structures in the Frank–Kasper (1958) sense, which means that any central increase in radius must be transmitted outward because there is no free space in the structure for the atoms to go to, much like in a continuous elastic medium. We still treat the central radius increase δR as associated with a change on one atom, but replace all the surroundings by a continuum. We consider whether this analogy with a continuous medium has anything to do with the A and B sites being elastically equivalent in the sense of § 1.

We apply the virial result (2.4) to our continuum model. We have to specify the forces F_i in (2.4) and the distances D_i at which they are applied and this can be done in two ways. Firstly, we may suppose that the continuum starts at R_A (for an A site), or some factor ρ times R_A which fixes D_i . We also suppose that the number of near neighbours to which the forces are applied is proportional to the area $4\pi(\rho R_A)^2$ of the sphere surrounding the sites: clearly a big atom has space for more neighbours as found in the Frank–Kasper phases. We again apply a force constant dependent on atomic size:

$$\lambda \propto (\rho R)^{-m} \quad (3.1)$$

and therefore write for the virial

$$\begin{aligned} \sum_i F_i D_i &= (\text{constant}) 4\pi(\rho R_A)^2 (\rho R_A)^{-m} (\rho R_A) \delta R_A \\ &= (\text{constant}) R_A^{3-m} \delta R_A \end{aligned} \quad (3.2)$$

and a corresponding expression for the B site. Clearly, from (1.8) and (2.4), for the two sites to be elastically equivalent [(1.11)] as required for the Pauling–Simon result, we require $m = 3$ in (3.2).

An alternative way of applying the continuum model would be to say that all the near neighbours

of the type A and B atoms are not at identically equal distances but are spread uniformly, *e.g.*, for the A sites, R_A taking values between $\rho_1 R_A$ and $\rho_2 R_A$, and similarly around the B sites. Again, with the same force law our virial for the expansion of an A site becomes

$$\begin{aligned} \sum_i F_i D_i &= \text{constant} \int_{\rho_1 R_A}^{\rho_2 R_A} 4\pi D^2 D^{-m} D \, dD \\ &= \text{constant} \int_{\rho_1 R_A}^{\rho_2 R_A} 4\pi D^{3-m} \, dD. \end{aligned} \quad (3.3)$$

For this to be the same for the A and B sites we need $m = 4$, in which case (3.3) becomes

$$\sum_i F_i D_i = (\text{constant}) 4\pi \ln(\rho_2/\rho_1). \quad (3.4)$$

We conclude therefore for this continuum analysis that we expect a value of m in the range 3 to 4 for consistency with the Pauling–Simon law.

4. Implications for the interatomic force law

We have seen in §§ 2 and 3 that the Pauling–Simon law cannot be ‘proved’ in some logical sense for the Laves phase and CaF_2 structures, unlike the situation for the CsCl , NaCl , NaTl and AuCu_3 structures which represent orderings on a set of identical sites. We have assumed harmonic interatomic forces with force constants λ_{AA} , λ_{AB} , λ_{BB} which depend on the atomic sizes and spacings according to

$$\lambda \propto D^{-m}. \quad (4.1)$$

To satisfy the Pauling–Simon law we required $m = 3.8$ and $m = 3.9$ in the atomistic calculations of § 2 for the two specific structures considered there, whereas our continuum approach of § 3 suggested $m = 3$ or $m = 4$ depending on how we applied it. The conclusion is that m must in general lie in the range 3 to 4.

What value of m might be expected? At first sight it might be thought that it is impossible to make general statements beyond the qualitative one that

large atoms might be expected to be softer, *i.e.* $m > 0$. However, our attention has been drawn to Badger’s rule, which effectively says $m = 3$, deduced empirically from the study of interatomic force constants in molecules (Badger, 1934). In this context we also refer to a theoretical discussion of Badger’s rule by Harris (1983). It is not possible to transfer either the empirical or the theoretical result blindly to the situation in a close-packed metal, but Badger’s rule does indicate that our value of m in the range 3 to 4 is indeed consistent with known systematic trends in interatomic force constants. In view of the insensitivity of the slope of the observed line in Figs. 1 and 2 to the exact value of γ in § 1, the difference between $m = 3$ and $m = 4$ does not make a large difference in fitting the data (Table 2).

We point out again that the force constant we are discussing relates to the near-neighbour atoms in contact and not to any indirect long-range effects. In metals it certainly includes electron gas contributions which strictly cannot be modelled as pair-wise forces. What we are discussing is how the strength of the force constant between near neighbours depends on the sizes of the atoms concerned.

We conclude therefore that there can be no general theoretical discussion of the Pauling–Simon law without some assumption about the interatomic force constants between different pairs of atoms. However, what is known of the systematic variation of force constants is such as to give the Pauling–Simon result or a very good approximation to it.

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