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Interatomic-Force Constants From a Central-Force Law

Abstract: Interatomic-force constants may be predicted from standard central-force laws using thermodynamic data. For the three cases where diffraction data are available (aluminum, copper, and iron) the predicted values agree within an order of magnitude for aluminum and iron, but differ strongly in the case of copper. It is suggested that Jacobsen's α_1, for copper, represents the strongest departure from a central-force model and should therefore be the most promising point for further theoretical work.

Introduction

The problem of calculating from first principles the effective potential of an atom or ion in a crystal lattice is an extremely difficult one and has yet to be satisfactorily treated.[1, 2] However, in view of the increasing availability of experimental data on the Born - von Kármán interatomic-force constants for some lattices,[3–5] it is of interest to see whether certain simple phenomenological potentials might not be used to represent results adequately to date and perhaps to act as a guide to future theory.

Of the many forms available,[6] two forms of a spherically symmetric, four-parameter, two-body potential which have been successfully used in thermodynamic studies are given in Eqs. (1) and (2):

$$\phi(r) = -\frac{a}{r^m} + \frac{b}{r^n} \qquad n>m \tag{1}$$

$$\phi(r) = -\frac{a}{r^{m'}} + be^{-r/\rho} \qquad r/\rho>0\,, \tag{2}$$

where a and b are constants of the system, r the nuclear separation and m, n, or m', ρ are adjustable parameters. These forms are purely heuristic, except perhaps for the exponential term in (2) which is suggested by quantum mechanics. These forms do not even permit prediction of the crystal structure, although they lead to a stable system if the structure is considered as a given parameter. However, the constants appearing in Eq. (1) have been evaluated by Fürth,[7] and Dayal and Sharma[8] for a great number of elements from thermodynamic data, and it is of interest to see if the same laws can yield the interatomic-force constants as given by x-ray and neutron-scattering experiments.

In the following sections we will consider the two specific forms, Eqs. (1) and (2), in some detail in order to get explicit numbers to compare with experiment, and then in the Discussion we will consider some general aspects of central forces.

Review of theory[9]

The inverse-power form, (1), is usually rewritten in terms of the pair equilibrium distance r_0' and potential depth μ'.

$$\phi(r) = \frac{mn}{n-m}\,\mu'\left[-\frac{1}{m}\left(\frac{r_0'}{r}\right)^m + \frac{1}{n}\left(\frac{r_0'}{r}\right)^n\right]. \tag{3}$$

Equation (3) is shown schematically in Fig. 1.

Although Fig. 1 represents the interaction of any two atoms in the lattice, it is not meant to represent their interaction if isolated from the lattice, in which case it may be radically different.

When particles are arranged in a three-dimensional array, the potential energy contributed to the lattice by an interior atom interacting with all of its neighbors becomes:

$$\Phi(r_1) = \frac{mn}{n-m}\,\mu'\left[-\frac{1}{m}\left(\frac{r_0'}{r_1}\right)^m S_m + \frac{1}{n}\left(\frac{r_0'}{r_1}\right)^n S_n\right], \tag{4}$$

where r_1 is the nearest neighbor distance and S_m, S_n are lattice sums of the form:

$$S_p = \sum_{j=1}^{\infty} g_j\left(\frac{1}{\sqrt{j}}\right)^p, \tag{5}$$

which have been evaluated by Misra[10] for simple cubic, fcc, and bcc arrays. The g_j's in the above expression represent the number of atoms which are a distance $r_1\sqrt{j}$ away from the origin atom; j takes on integral values for fcc and simple cubic lattices. The value of the sum (5) decreases with increasing power p, but never gets smaller than g_1, the number of first neighbors, nor gets much larger than twice this value for the smallest power considered.

The pair parameters, r_0' and μ', are usually replaced by lattice parameters through the following:

a) The value of r_1, say r_{10}, which makes $\Phi(r_1)$ a minimum is readily obtainable by setting $d\Phi(r_1)/dr_1=0$ and solving for r_{10}. This value, r_{10}, is the static lattice nearest-neighbor spacing, and is, to a first approximation, the observed spacing. For potential (1):

$$\frac{r_0'}{r_{10}}=\left(\frac{S_m}{S_n}\right)^{1/n-m}. \tag{6}$$

Taking the published values of Dayal and Sharma: $S_m\approx 2S_n$, $n=7$, $m=4$, we see that $r_0'=(2)^{1/3}r_{10}$, and thus the nearest neighbor is pushed considerably closer[11] than the equilibrium distance by the attraction of the farther neighbors to the origin atom (see Fig. 1).

b) The total binding energy of the lattice for $r_1=r_{10}$ should equal the heat of dissociation (neglecting the usually small correction for the thermal energy[1]):

$$\lambda=-\frac{1}{2}N\Phi(r_{10}),$$

where λ is the heat of dissociation per mole and $N=$ Avagadro's number. We then obtain for μ':

$$\mu'=\frac{2\lambda}{N}\bigg/S_m\left(\frac{S_m}{S_n}\right)^{m/n-m}. \tag{7}$$

Equation (4) may now be rewritten in terms of r_{10} and λ and becomes:

$$\Phi(r_1)=\left(\frac{2\lambda}{N}\right)\frac{mn}{n-m}\left[-\frac{1}{m}\left(\frac{r_{10}}{r_1}\right)^m+\frac{1}{n}\left(\frac{r_{10}}{r_1}\right)^n\right].$$

This equation is shown schematically in Fig. 2, and is the same curve as Fig. 1, except for the value of r at which it has its minimum. In Fig. 1, r_0' is the atom-pair distance for minimum pair energy, whereas r_{10} (Fig. 2) is the atom-pair distance for minimum total lattice energy.

The constants m and n are usually evaluated for the so-called static lattice, a fictitious absolute zero, where all parameters have their room-temperature behavior merely extrapolated to $T=0$. Although Dayal and Sharma, and Fürth, use more elaborate developments, one may essentially take for the equation of state:

$$P=-\frac{1}{2}\left(\frac{\partial\Phi}{\partial V}\right)_T,$$

where P and V are pressure and volume, respectively. From this are obtained relations for compressibility such as:

$$\frac{1}{k_0}=-V_0\left(\frac{\partial p}{\partial V}\right)_0=\frac{\lambda}{9V_0}mn$$

and

$$\frac{1}{k_0^2}\left(\frac{\partial k}{\partial P}\right)_0=-\frac{m+n+9}{3},$$

from which m and n may be evaluated.

Figure 1 **Isolated-pair central-force potential.**

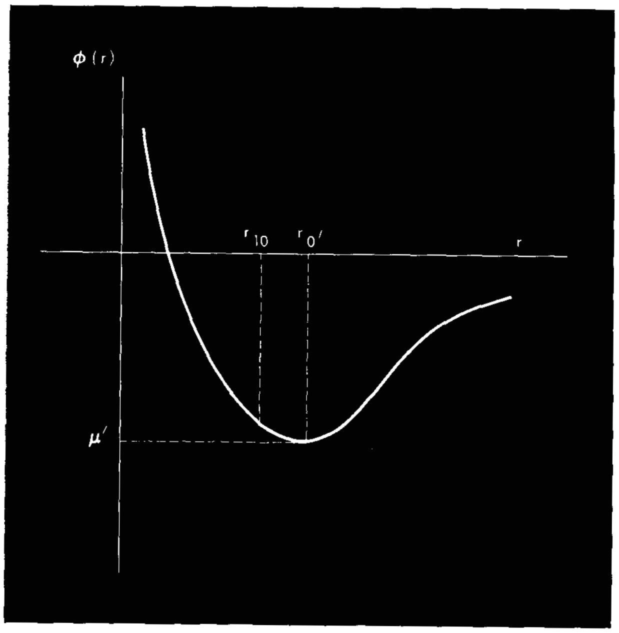
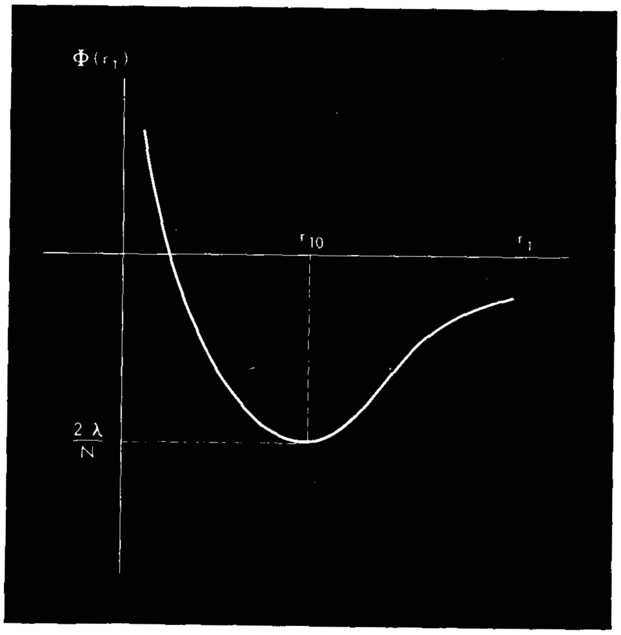


Figure 2 **Lattice potential, central-force model.** *(r_1 is nearest-neighbor distance.)*



Results with inverse-power law

We may now rewrite (3), using (6) and (7), in terms of r_{10} and λ and treat the potential as representing that describing the interaction between a pair of atoms in the lattice. Thus the lattice-pair potential becomes:

$$\phi(r)=\frac{2\lambda}{N}\frac{mn}{n-m}\left[-\frac{1}{m}\left(\frac{r_{10}}{r}\right)^m\frac{1}{S_m}+\frac{1}{n}\left(\frac{r_{10}}{r}\right)^n\frac{1}{S_n}\right], \quad (8)$$

which is again represented by the curve in Fig. 1.

One may now calculate the forces which a lattice pair exert on each other in the usual way:

$$\mathbf{F}_r=-\frac{\partial\phi(r)}{\partial r}\boldsymbol{\mu}_r=\frac{2\lambda}{N}\frac{mn}{n-m}\left[-\frac{1}{S_m}\frac{r_{10}{}^m}{r^{m+2}}+\frac{1}{S_n}\frac{r_{10}{}^n}{r^{n+2}}\right]\mathbf{r}. \quad (9)$$

Each atom exerts some force on every other atom, even if all atoms are in their equilibrium positions. Expressing the force as a vector sum of its x, y, and z components, the interatomic-force constants are defined as the negatives of the partials in the following array:

$$dF_x=\left(\frac{\partial F_x}{\partial x}\right)dx+\left(\frac{\partial F_x}{\partial y}\right)dy+\left(\frac{\partial F_x}{\partial z}\right)dz$$

$$dF_y=\left(\frac{\partial F_y}{\partial x}\right)dx+\left(\frac{\partial F_y}{\partial y}\right)dy+\left(\frac{\partial F_y}{\partial z}\right)dz$$

$$dF_z=\left(\frac{\partial F_z}{\partial x}\right)dx+\left(\frac{\partial F_z}{\partial y}\right)dy+\left(\frac{\partial F_z}{\partial z}\right)dz\,. \quad (10)$$

The partials, and therefore the interatomic-force constants, are actually, as is well known, the second derivatives of the potential.

The nine interatomic-force constants needed to describe the forces between a pair of atoms due to relative displacement dx, dy, dz is reduced in number by the crystal symmetry. Thus, for example, the array describing the interaction between the origin atom and a first neighbor at position $x=a/2$, $y=0$, $z=a/2$ in a fcc lattice is (from Walker[3]):

$$D(\tfrac{1}{2}0\tfrac{1}{2})=\begin{pmatrix}\alpha_1 & 0 & \gamma_1\\ 0 & \beta_1 & 0\\ \gamma_1 & 0 & \alpha_1\end{pmatrix}.$$

Walker's symbols, in our notation, are:

$$\alpha_1=-\left(\frac{\partial F_x}{\partial x}\right)=-\left(\frac{\partial F_z}{\partial z}\right),\ \beta_1=-\left(\frac{\partial F_y}{\partial y}\right);$$

$$\gamma_1=-\left(\frac{\partial F_x}{\partial z}\right)=-\left(\frac{\partial F_z}{\partial x}\right);$$

and all other partials are zero. That this is actually the case is easily seen by taking the proper derivatives of (9):

$$\frac{\partial F_x}{\partial x}=\frac{2\lambda}{N}\frac{mn}{n-m}\left[-\frac{1}{S_m}\frac{r_{10}{}^m}{r^{m+2}}+\frac{1}{S_n}\frac{r_{10}{}^n}{r^{n+2}}+\frac{(m+2)}{S_m}\frac{r_{10}{}^m x^2}{r^{m+4}}-\frac{(n+2)}{S_n}\frac{r_{10}{}^n x^2}{r^{n+4}}\right] \quad (11)$$

$$\frac{\partial F_x}{\partial y}=\frac{2\lambda}{N}\frac{mn}{n-m}\left[\frac{(m+2)}{S_m}\frac{r_{10}{}^m xy}{r^{m+4}}-\frac{(n+2)}{S_n}\frac{r_{10}{}^n xy}{r^{n+4}}\right] \quad (12)$$

and using the known values for x, y, z. We need list only two of the derivatives in detail, since all others may be obtained from these by interchanging x, y, z. The relationships derived on the basis of a central force will contain the proper identities, since the force contains all the necessary symmetries in these simple cases.

Each author adopts his own list of symbols for the interatomic-force constants. Walker's D symbol (see above) is very convenient: $D(xyz)ij$; the x, y, z are the coordinates of the neighbors in question with respect to an atom at the origin of the standard crystallographic cell, and ij indicates which partial derivative is required. With a list of atomic coordinates and Eqs. (11) and (12), an expression can easily be written out for any particular interatomic-force constant in any simple structure. If the lattice sums have been evaluated, and m, n, r_{10}, λ are known, then the value of the force constant can be predicted within the assumptions used in the derivation.

In Table 1 are listed the definitions of the symbols used and the values of the interatomic-force constants reported by the various authors listed in References 3, 4, and 5, for first and second neighbors. Third neighbors have not been listed, even though reported, because neither the experimental numbers nor the potential curve is thought to be very satisfactory at this distance. The calculated values, based on the formulas above, and the data in Table 2 taken from Dayal and Sharma, and Fürth, are listed in the next column.

For aluminum and iron the calculated values agree with the experimental values within an order of magnitude, and have the same sign. For copper there is violent disagreement in the case of α_1, at least in the sign of the term, and practically no fit for second neighbors.

Results with exponential law

It is tempting to see if a better fit could be obtained by using the exponential form of the repulsive potential (2), if a suitable approximation could be made in the mathematics.

Equation (2) may be rewritten in terms of r_0'' and μ'', the pair equilibrium constants, and becomes:

$$\phi(r)=\frac{m'\eta}{\eta-m'}\mu''\left\{-\frac{1}{m'}\left(\frac{r_0''}{r}\right)^{m'}+\frac{1}{\eta}\exp\left[-\eta\left(\frac{r}{r_0''}-1\right)\right]\right\} \quad (13)$$

if we set $r_0''/\rho\equiv\eta$.

Table 1 **Comparison of experimental force constants and values calculated from central-force laws.**

Force Constants	*Al**	*Experiment†*	*Inverse-Power Law*	*Exponential Law*
$D(\frac{1}{2}\,0\,\frac{1}{2})_{11} = -\frac{\partial F_x}{\partial x}$	α_1	8.45	18.6	19.8
$D(\frac{1}{2}\,0\,\frac{1}{2})_{22} = -\frac{\partial F_y}{\partial y}$	β_1	−.93	−3.9	−4.1
$D(\frac{1}{2}\,0\,\frac{1}{2})_{13} = -\frac{\partial F_x}{\partial z}$	γ_1	10.67	22.5	24.1
$D(1\,0\,0)_{11} = -\frac{\partial F_x}{\partial x}$	$\alpha_{2'}$	2.14	.5	.4
$D(1\,0\,0)_{22} = -\frac{\partial F_y}{\partial y}$	β_2	.40	.13	.02
	*Fe**			
$D(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})_{11} = -\frac{\partial F_x}{\partial x}$	α	11.7	27.6	28.7
$D(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})_{12} = -\frac{\partial F_x}{\partial y}$	β	11.9	37.0	38.8
$D(1\,0\,0)_{11} = -\frac{\partial F_x}{\partial x}$	α'	11.6	21.2	23.8
$D(1\,0\,0)_{12} = -\frac{\partial F_y}{\partial y}$	β'	−2.5	−1.25	−1.0
	*Cu**			
$D(\frac{1}{2}\,0\,\frac{1}{2})_{11} = -\frac{\partial F_x}{\partial x}$	β_1	8.7	29.8	30.3
$D(\frac{1}{2}\,0\,\frac{1}{2})_{22} = -\frac{\partial F_y}{\partial y}$	α_1	4.8	−5.7	−6.4
$D(\frac{1}{2}\,0\,\frac{1}{2})_{13} = -\frac{\partial F_x}{\partial z}$	γ_1	12.5	35.6	36.7
$D(1\,0\,0)_{11} = -\frac{\partial F_x}{\partial x}$	α_2	3.50	.3	.6
$D(1\,0\,0)_{22} = -\frac{\partial F_y}{\partial y}$	β_2	−.70	.26	.02

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*Symbols used by author reporting data.
†In units of 10^3 dynes/cm.

Table 2 **Values of constants of central-force, inverse-power law from Dayal and Sharma, and Fürth.**

Element	$\lambda \frac{\text{Kcal}}{\text{gm-atom}}$	$V_0 cm^3$	m	n
Al	67.6	10.025	4	6.5
Fe	96.5	7.16	4	7
Cu	81.7	7.1	4	7

The total potential energy of the lattice becomes:

$$\frac{1}{2}\Phi(r_1)=\frac{1}{2}\frac{m'\eta}{\eta-m'}\mu''\left\{-\frac{1}{m'}\left(\frac{r_0''}{r_1}\right)^{m'}S_{m'}\right.$$
$$\left.+\frac{1}{\eta}\sum_j g_j\exp\left[-\eta\left(\frac{r_1\sqrt{j}}{r_0''}-1\right)\right]\right\}. \tag{14}$$

Setting $\frac{d\Phi}{dr_1}=0$ for $r_1=r_{10}$ gives:

$$\left(\frac{r_0''}{r_{10}}\right)^{m'+1}=\frac{1}{S_{m'}}\sum_j g_j\sqrt{j}$$
$$\exp\left[-\eta\left(\frac{r_{10}}{r_0''}\sqrt{j}-1\right)\right]. \tag{15}$$

This transcendental equation blocks further analytical results.

If, for convenience, we write $R=\frac{r_0''}{r_{10}}$ and recall that we expect $R>1$, then if η is of the order of magnitude of 10, the $j=1$ term is by far the dominant one. In that case we shall make the following approximation:

$$S_{m'}R^{m'+1}=\sum_j g_j\sqrt{j}\exp\left[-\eta\left(\frac{\sqrt{j}}{R}-1\right)\right]$$
$$\cong\sum_j g_j\exp\left[-\eta\left(\frac{\sqrt{j}}{R}-1\right)\right]. \tag{16}$$

On the basis of the above, which is somewhat equivalent to assuming only first-neighbor repulsive interaction in the evaluation of R, we obtain:

$$\mu''=\frac{2\lambda}{N}\frac{(\eta-m')}{(\eta-m'R)S_{m'}R^{m'}}. \tag{17}$$

To get some idea of what values m' and η might take, we recall that they are determined by the behavior of $\Phi(r_1)$ near $r_1=r_{10}$;

$$\frac{d\Phi(r_1)}{dr_1}=0,$$

despite the approximation made in (16). Deriving analogous compressibility relations and using the same data from which m and n were evaluated previously, we have two sets of values:

(1) $m'=3.1$, $(\eta/R)=10.5$ and

(2) $m'=9$, $(\eta/R)=2.6$.

The first is consistent with our assumptions.

Making the further substitutions that

$$n'\equiv\eta/R=\frac{r_{10}}{\rho}$$

and

$$S_{m'}R^{m'+1}\equiv S_{n'}e^{n'R}$$

we can write for the lattice-pair potential:

$$\phi(r)=\frac{2\lambda}{N}\frac{m'n'}{n'-m'}\left[-\frac{1}{m'}\left(\frac{r_{10}}{r}\right)^{m'}\frac{1}{S_{m'}}\right.$$
$$\left.+\frac{1}{n'}\frac{\exp\left[-n'(r/r_{10})\right]}{S_{n'}}\right]. \tag{18}$$

Since $S_{n'}e^{n'}\cong g_1\cong S_n$ for all practical purposes, for first and second neighbors, the exponential law produces no startling differences in the interatomic-force constants. The last column in Table 1 lists the values obtained by using the above expressions and $m'=3.1$, $n'=10.5$.

Discussion and conclusions

The specific central-force laws considered, with constants evaluated from thermodynamic data, predict interatomic-force constants for first and second neighbors which agree qualitatively with experimental values for Al and Fe, but which disagree strongly for the case of Cu. Although it is impossible to conclude that the inverse-power law with constants as given is a satisfactory heuristic potential for Al or Fe, nonetheless certain irreconcilable features between the observed force constants for Al and Fe on the one hand, and Cu on the other, suggest that Cu is far less "central like." For any central-force system we may write:

$$-d\mathbf{F}=f_1(r)d\mathbf{r}+\mathbf{r}f_2(r)\mathbf{r}\cdot d\mathbf{r}, \tag{19}$$

where $f_1(r)$ is proportional to $d\phi(r)/dr$ and $f_2(r)$ contains second derivatives as well (Eqs. (11) and (12) are explicit forms of this relationship for the inverse-power law). If, for example, in the previous sections, r_{10} were assumed to be the pair equilibrium position, then $d\phi(r)/dr$ at $r=r_{10}$ would be zero for the first neighbors and $f_1(r)=0$. This condition leads to what is generally called the "Born Central Field" and to the following identities for fcc:

$D(\tfrac{1}{2}0\tfrac{1}{2})_{22}=0$

$D(\tfrac{1}{2}0\tfrac{1}{2})_{11}=D(\tfrac{1}{2}0\tfrac{1}{2})_{13}$

$D(100)_{22}=0$;

for bcc:

$D(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})_{11}=D(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})_{12}$

$D(100)_{22}=0$.

Thus the inclusion of the fact that first neighbors are not at the pair equilibrium position leads to more detail in the predicted constants. The predicted value of β_1 for Al and α_1 for Cu depends explicitly on the fact that $d\phi(r)/dr\neq0$ at $r=r_{10}$. From Fig. 1 we see that the slope is negative at $r=r_{10}$, leading to a negative force constant, and in order to have a positive α_1 for Cu, it would be necessary that $r_{10}>r_0'$. This would imply a repulsive force of longer range than the attractive force, contrary to all physical reasoning. We may therefore conclude that for Cu it would be impossible to discover a central-force law which would predict, for the static lattice, force constants equal to the experimentally determined force constants.

Table 3 **Elastic constants in units of 10^{12} dynes/cm^2.**

Element	C_{11}	C_{12}	C_{44}
Fe	2.37	1.41	1.16
Al	1.08	.62	.28
Cu	1.68	1.21	.75

The Cauchy condition that $C_{12}=C_{44}$ has been shown to follow from the central-force assumption[12] for these elements. From Table 3 it can be seen that the above results were perhaps to be expected for Cu and Fe, but what is unexpected is that the constants for Al are given so well by the inverse-power law. Only a small modification is needed in the inverse-power law constants to change the first-neighbor force constants by a factor of two to bring them more in line with the experimental values. Thermal expansion, leading to a larger r_{10}, would lower all values; however, the change in r_{10} should not be greater than 0.5% over the temperature range. A dynamical r_{10} due to the thermal notion should be nearer to r_0' and could easily change the first-neighbor constants by the desired amounts. Thus it probably would be in the second- or farther-neighbor interaction that the important part of the noncentral nature of the force would appear.

The question of how far out the potential curve one should be willing to venture in calculating force constants for further neighbors is of some interest and can perhaps be approached through the relationship between the experimental elastic constants and sums of the force constants. These relationships are derived by using the method of long waves in the Born-von Kármán theory. For a fcc lattice they become, for example:

$$aC_{11}=4\alpha_1+4\alpha_2+16\alpha_3+8\beta_3+\cdots$$

$$aC_{44}=2\alpha_1+2\beta_1+4\beta_2+4\alpha_3+20\beta_3+\cdots$$

$$a(C_{12}+C_{44})=4\gamma_1+8\gamma_3+32\delta_3+\cdots$$

in which Walker's symbols are used, and where a is the lattice parameter. The experimental force constants satisfy this consistency check with the elastic constants by the time third neighbors are reached. The force constants predicted by the inverse-power law require consideration of further neighbors before converging.

Although the results of this paper bear out the contention that a simple phenomenological central-force law is not adequate to describe in detail the atomic interactions in simple metals, still it is gratifying to note that the predicted values are, more often than not, within an order of magnitude of the observed values. The strong departures should serve as guides for the development of more satisfactory theories.

References

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11. This is not always the case experimentally. See, for example, Slater, *Introduction to Chemical Physics,* Table on p. 455, where interatomic distances in the gases and solid phases are compared for the alkali elements. However, whether or not the isolated atom pairs actually obey the same potential as they do in the lattice is immaterial to the development of the model.
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Revised manuscript received December 8, 1958