

# DISTRIBUTION OF THE LATTICE ENERGY IN CUBIC CRYSTALS AND ITS VARIATION WITH COMPRESSION OR EXPANSION\*

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**Abstract**—The total lattice energy of face-centred and body-centred cubic crystals has been calculated on the assumption of a pair-wise interaction potential, for a variety of such potentials. These were either of Morse or Mie (Lennard-Jones) type, with the parameters adjusted to minimize the total lattice energy for an ideal unstrained crystal at 0°K. The same potentials were used to compute the variation in lattice energy when the lattice is allowed to expand or contract by up to 2.5 per cent. The relative contributions of different interactions to the total energy are given. For face-centred cubic crystals, most potentials predict a major contribution from nearest-neighbour interactions, although the contributions of second and higher neighbours are still significant. For body-centred cubic crystals, the dominant contribution usually comes from the second neighbour interactions. Some typical variations in these contributions with changes in lattice parameter are given.

## 1. INTRODUCTION

IN THIS paper, we assume that the total lattice energy (cohesive energy) of a crystal can be calculated as the sum of pair-wise interactions between all atoms. Various forms are considered for the interaction potential function, in all of which the parameters have been adjusted to minimize the lattice energy for an ideal unstrained crystal at 0°K. The lattice energy is then calculated for body-centred and face-centred cubic crystals, first for a lattice parameter corresponding to this minimum energy and then also for parameters deviating from this value by a few per cent. Such changes in lattice energy may be expected if the crystal is at higher temperatures or under hydrostatic pressure. Clearly any vibrational contribution to the lattice energy is not taken into account in this calculation. Corresponding calculations of

surface energy are discussed in the following paper.<sup>(1)</sup>

The calculation of energies by summing pair-wise interactions has been used previously by many authors,<sup>(2,3)</sup> despite the recognition that many-body interactions may make a significant contribution to the total energy.<sup>(4)</sup> The attractions of the method are that it is mathematically tractable and that it does appear to provide a good approximation in many cases. The pair-wise potential itself can be chosen either as a "real" potential derived from quantum-mechanical calculations or as a "fictitious" potential<sup>(2)</sup> of simple mathematical form and containing one or more adjustable parameters. The second approach is more in keeping with the philosophy of the method and may be expected to give a better approximation when the parameters are chosen to fit some specific experimental data.

As discussed in detail in Section 2, we have restricted our calculations to Morse and Mie

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(Lennard-Jones) potentials without any truncation of the potential. Truncation, which corresponds to considering only, say, the first three or four shells of neighbours, involves an extra assumption that is unnecessary when high-speed computers are available and highly undesirable when more than one crystal structure is being considered for the same potential. Thus our calculations give *precise* results for ideal crystals interacting with potentials of the *precise* form given in equations (2) or (3).

We considered using also oscillatory potentials such as have been discussed recently,<sup>(5-8)</sup> but did not pursue this investigation for the following reasons:

(i) The only explicit potentials available are those of JOHNSON, HUTCHINSON and MARCH,<sup>(7)</sup> and since these involve a number of parameters derived specifically for each metal, generalizations become very difficult.

(ii) In some associated calculations on surface energy,<sup>(9)</sup> out of the seven potentials available for cubic metals, one was divergent, one gave negative values of surface energy and a third gave a degree of anisotropy of more than 3, which is very much greater than that found by any other calculation or experiment.

## 2. METHOD OF CALCULATION

If the interaction energy of two atoms at a distance,  $r$ , is given by  $E(r)$ , then, for a perfect infinite crystal, the total lattice energy per atom is given by

$$E_G = \frac{1}{2} \sum_i M_i E(r_i), \quad (1)$$

where  $r_i$  is an interatomic distance,  $M_i$  is the number of neighbours of a given atom at this distance, and the sum extends over all possible  $r_i$ . The method of calculation is therefore simply to list for each structure the possible values of  $r_i$  and their associated multiplicities  $M_i$ , and then evaluate the lattice sum for particular potential functions  $E(r)$ . This corresponds to rewriting equation (1) in the form

$$E_G = \sum_i E_i^S, \quad (2)$$

where

$$E_i^S = \frac{1}{2} M_i E(r_i) \quad (3)$$

represents the contribution to the lattice energy from the  $i$ -th shell of neighbours.

The potentials considered were either Morse potentials of the form

$$E(r)/E_0 = [1 - \exp\{-a(r-r_0)/r_0\}]^2 - 1, \quad (4)$$

or Mie (Lennard-Jones) potentials of the form

$$E(r)/E_0 = \{n(r_0/r)^m - m(r_0/r)^n\}/(m-n), \quad (5)$$

where, in all potentials,  $E_0$  corresponds to the maximum interaction energy which occurs at a separation  $r_0$ .

Calculations were made for various values of the Morse constant  $a$  between 3 and 6, while for the Mie functions the attractive exponent  $m$  varied from 4.5 to 9 and the repulsive exponent  $n$  (always greater than  $m$ ) ranged from 6 to 14. The scaling factors  $E_0$  were left arbitrary since only relative energy values are considered but the  $r_0$  values were adjusted, as described below, to produce a minimum  $E_G$  for given  $a$  or  $(m, n)$ . Figure 1 shows some Morse functions, while some typical Mie functions are plotted in the following paper (1) in comparison with a Morse function with  $a = 4$ .

All summations with Morse potentials were carried through for the first 300 different values of  $r_i$ , i.e. for the first 300 shells of neighbours. This corresponds to considering all interactions out to 17-18 times  $r_1$ , and ensured that all energy values were correct to at least 8 significant figures. For Mie potentials, the initial summations were carried through for 500 shells of neighbours and the effects of more distant interactions taken into account by means of an integral approximation so that the overall accuracy should be comparable to that for the Morse potentials.

### (a) Relation between the lattice parameter and $r_0$

From equations (4) and (5) it can be seen that distances enter only through the dimensionless variable  $(r/r_0)$ , while distances in the crystal are available in terms of the lattice parameter or of the nearest-neighbour distance,  $r_1$ . Thus, in order to calculate the sums, the ratio  $r_1/r_0$  must be specified so that we can write

$$r/r_0 = (r/r_1) \cdot (r_1/r_0). \quad (6)$$

Then, for the interatomic distances  $r_i$ , the ratios  $b_i = r_i/r_1$  are fixed and known for a particular

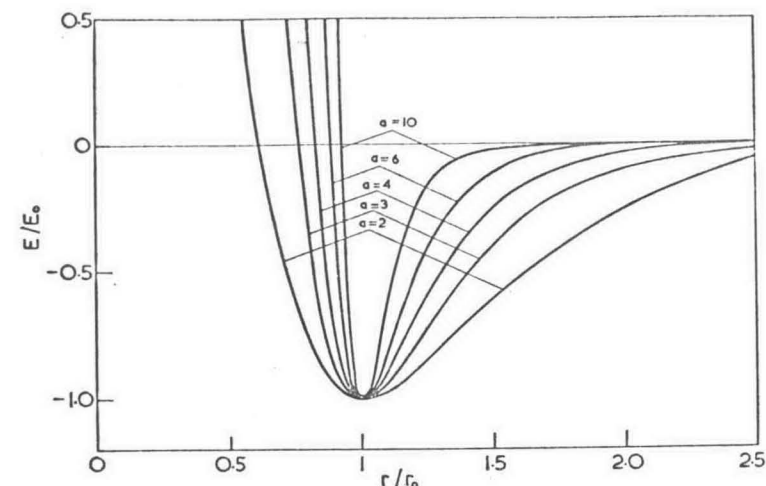


FIG. 1. Morse functions for various values of the Morse constant  $a$ .

lattice, e.g. for the body-centred cubic lattice,  $b_1 = 1$ ,  $b_2 = 2/\sqrt{3}$ ,  $b_3 = \sqrt{8/3}$ , etc., and  $r/r_0$  is now determinate.

In this notation, the lattice energy with a Mie potential is

$$E_G = \frac{E_0}{2} \{n(r_0/r_1)^m S(m) - m(r_0/r_1)^n S(n)\}/(m-n), \quad (7)$$

where

$$S(j) = \sum_i M_i b_i^{-j}. \quad (8)$$

Then, minimum  $E_G$  is easily shown to occur for  $r_1 = r_1^*$ , where

$$(r_0/r_1^*) = \{S(m)/S(n)\}^{1/(n-m)}. \quad (9)$$

The lattice sums  $S(j)$  have been calculated by JONES and INGHAM<sup>(10)</sup> for all integral  $j$  from 4 to 30 and appear in their Table 1 as  $B_j$  for the body-centred cubic and  $C_j$  for the face-centred cubic lattice. Since we wished to use some half-integral exponents we have recalculated  $S(j)$  for all integral and half-integral values from 3.5 to 20. Values of  $(r_0/r_1^*)$  are given in Table 1 for various values of  $(m, n)$ .

For the Morse potentials, a similar procedure can be followed but  $(r_0/r_1^*)$  cannot be evaluated in terms of simple lattice sums and a numerical minimization procedure is necessary. The values of

$(r_0/r_1^*)$  appropriate to various Morse constants  $a$  are also given in Table 1.

It may be noted here that GIRIFALCO and WEIZER<sup>(3)</sup> have considered a range of materials and used experimental values of sublimation energy, lattice parameter, and compressibility to deduce the values of  $E_0$ ,  $a$ , and  $r_0$  appropriate to each. Table 2 lists these as some of our calculations have been carried through with them. Although they express the Morse potential in a different form their values correspond to the same minimization criterion that we have used. Other workers have used a similar approach to deduce the  $(m, n)$  values of Mie potentials appropriate to different materials.<sup>(2)</sup> Some discussion of this appears in Section 4(b) of the following paper.<sup>(1)</sup>

### (b) Variation of the lattice parameter

In studying the effect of temperature or pressure on the lattice energy, we assume that the nearest-neighbour distance in a perfect unstrained crystal at 0°K is  $r_1^*$  and that the only effect of temperature or pressure is to vary the  $r_1$  by a few per cent from this value. The sums such as those in equation (5) can then be evaluated to show the variation in lattice energy with lattice parameter. This has been carried out for  $r_1/r_1^*$  deviating from unity by up to  $\pm 2.5$  per cent for the Mie potentials and up to  $\pm 5$  per cent for the Morse potentials.

In order that the variation in  $E_G$ , expressed here in terms of a variation in lattice parameter, can be

Table 1. Ratio of the nearest-neighbour distance,  $r_1^*$ , for minimum lattice energy to the distance of the minimum in the potential function,  $r_0$ . For ratios of lattice parameter to  $r_0$ , the values given must be multiplied by  $\sqrt{2}$  for face-centred cubic and  $2/\sqrt{3}$  for body-centred cubic crystals

Face-centred cubic							
Morse $a$	=	3	3.5	4	4.5	5	6
$r_1^*/r_0$		0.6346	0.8266	0.9014	0.9395	0.9612	0.9825
Mie $m$	=	4.5	5	6	7	8	9
$n$	=	6	7	8	10	12	14
		0.8140	0.8519	0.9243	0.9411	0.9583	0.9806
		0.8564	0.8873	0.9243	0.9411	0.9583	0.9806
		0.8844	0.9104	0.9411	0.9583	0.9806	0.9855
		0.9182	0.9379	0.9607	0.9731	0.9806	0.9855
		0.9375	0.9532	0.9712	0.9809	0.9866	0.9903
		0.9497	0.9628	0.9776	0.9855	0.9901	0.9930

Body-centred cubic							
Morse $a$	=	3	3.5	4	4.5	5	6
$r_1^*/r_0$		0.6167	0.8035	0.8767	0.9147	0.9367	0.9601
Mie $m$	=	4.5	5	6	7	8	9
$n$	=	6	7	8	10	12	14
		0.7932	0.8303	0.9021	0.9193	0.9368	0.9611
		0.8351	0.8655	0.9021	0.9193	0.9368	0.9611
		0.8629	0.8886	0.9193	0.9368	0.9529	0.9611
		0.8974	0.9169	0.9399	0.9529	0.9611	0.9666
		0.9178	0.9335	0.9519	0.9621	0.9686	0.9730
		0.9312	0.9444	0.9597	0.9682	0.9736	0.9772

Table 3. Temperatures and pressure necessary to change lattice parameters by particular amounts<sup>(11,12)</sup>

Material	Temperature (°K) at which the lattice parameter exceeds 0°K value by		Pressure (10 <sup>3</sup> kg/cm <sup>2</sup> ) which changes the lattice parameter at room temperature by		
	1 per cent	2 per cent	-0.5 per cent	-1 per cent	-2 per cent
Na	180	350	1.0	2.0	4.2
Al	450	800	11.5	25	57
Cu	650	1250	23.5	53	~200
W	1950	3250	70	—	—

considered in terms of temperature or pressure, Table 3 gives the relevant experimental data for a few metals.

### 3. RESULTS

Table 4 shows the calculated lattice energy for various potentials together with the variations

expected for 1 per cent and 2 per cent change in parameter.

Since  $E_G$  has been minimized at  $r_1^*$ , the changes in the total lattice energy are all small but much greater changes occur in the energies associated with the interactions of particular atoms or groups of atoms. Thus, Fig. 2 shows, for a Morse  $a = 4$

Table 2. Constants in the Morse potential as deduced by GIRIFALCO and WEIZER.<sup>(3)</sup> The expressions in brackets use the symbols from (3)

Metal	Face-centred cubic crystals							Body-centred cubic crystals								
	Pb	Ag	Ni	Cu	Al	Ca	Sr	Mo	Cr	W	Fe	Ba	K	Na	Cs	Rb
$E_0(=D)$ , in eV	0.2348	0.3323	0.4205	0.3429	0.2703	0.1623	0.1513	0.8032	0.4414	0.9906	0.4174	0.1416	0.05424	0.06334	0.04485	0.04644
$a(= \ln \beta)$	4.419	4.265	3.947	3.894	3.788	3.680	3.680	4.488	4.330	4.279	3.951	3.530	3.170	3.148	3.142	3.098
$r_1^*/r_0(= \sqrt{2\alpha a_0}/\ln \beta)$	0.9348	0.9244	0.8958	0.8898	0.8762	0.8602	0.8602	0.9140	0.9041	0.9006	0.8716	0.8096	0.7065	0.6972	0.6947	0.6743
$E_0(=D)$ , in eV	0.8032	0.4414	0.9906	0.4174	0.1416	0.05424	0.06334	0.8032	0.4414	0.9906	0.4174	0.1416	0.05424	0.06334	0.04485	0.04644
$a(= \ln \beta)$	4.488	4.330	4.279	3.951	3.530	3.170	3.148	4.488	4.330	4.279	3.951	3.530	3.170	3.148	3.142	3.098
$r_1^*/r_0(= \sqrt{3\alpha a_0}/\ln \beta)$	0.9140	0.9041	0.9006	0.8716	0.8096	0.7065	0.6972	0.9140	0.9041	0.9006	0.8716	0.8096	0.7065	0.6972	0.6947	0.6743

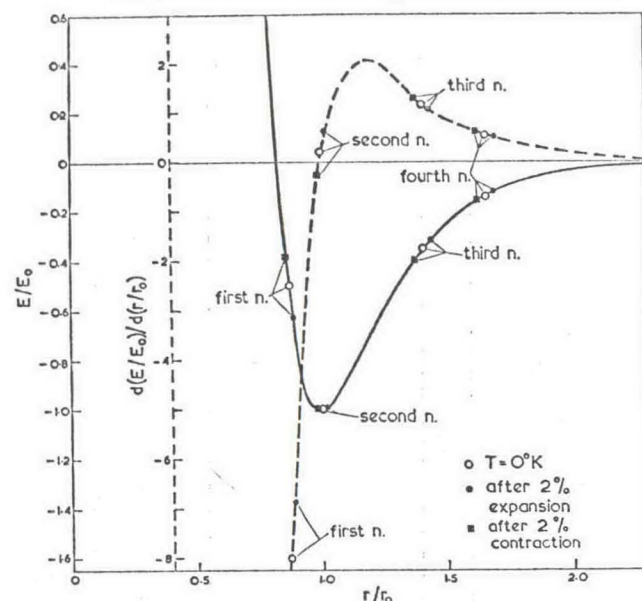


FIG. 2. Interaction energy (full line) between, and force exerted on (broken line) first to fourth nearest neighbours in a body-centred cubic crystal with a Morse  $a = 4$  potential. The changes caused by a 2 per cent lattice expansion or contraction are also shown.

Table 4. Lattice energies,  $E_G$  for different potentials and the differences caused by small variations of the lattice parameter from its value for minimum  $E_G$ . Since  $E_G$  is itself negative, the quoted increases are in fact decreases in the absolute value of  $E_G$ .

Potential	$-E_G/E_0$		Per cent increase in $E_G$ for lattice expansion of contraction of			
	f.c.c.	b.c.c.	1 per cent	2 per cent	1 per cent	2 per cent
Morse: $a =$						
3	22.802	22.806	0.04	0.17	0.05	0.19
3.25	15.895	15.881	0.07	0.27	0.07	0.30
3.5	12.819	12.788	0.09	0.35	0.10	0.40
3.75	11.049	11.000	0.11	0.44	0.12	0.50
4	9.900	9.830	0.13	0.52	0.15	0.60
4.25	9.097	9.007	0.16	0.60	0.17	0.71
4.5	8.509	8.397	0.18	0.69	0.20	0.82
4.75	8.064	7.927	0.20	0.78	0.22	0.93
5	7.718	7.555	0.23	0.87	0.25	1.05
5.25	7.443	7.253	0.25	0.96	0.28	1.18
5.5	7.222	7.003	0.28	1.06	0.31	1.31
5.75	7.041	6.793	0.31	1.15	0.34	1.45
6	6.892	6.612	0.33	1.26	0.38	1.59
Mie: $(m, n) =$						
(4.5, 6)	24.840	24.609	0.13	0.49	0.14	0.59
(4.5, 14)	12.410	11.951	0.29	1.10	0.34	1.46
(5, 7)	15.423	15.198	0.17	0.63	0.18	0.77
(5, 8)	13.567	13.319	0.19	0.72	0.21	0.89
(6, 12)	8.610	8.237	0.34	1.26	0.39	1.66
(9, 14)	6.656	6.089	0.58	2.13	0.69	3.01

potential in a body-centred cubic crystal, how the energies of interaction between first to fourth nearest-neighbours are related for  $r_1/r_1^* = 0.98, 1.0, \text{ and } 1.02$ . The derivative of this energy, which gives the force on one atom exerted by the appropriate neighbours, is also plotted here. More details of these energies are given in Fig. 3 for a variety of Morse constants, while Fig. 4 shows the variation with parameter of  $E(r_1)/E(r_2)$ . Figure 5 shows  $E_i^s$  ( $i = 1, \dots, 4$ ) as functions of the parameter for two different Morse constants.

#### 4. DISCUSSION OF THE RESULTS

Although the variation of  $E_G$  with lattice parameter, as shown in Table 4, is in fact small, the following generalizations are of interest.

(i) The fractional change in  $E_G$  for a given change in parameter and given potential is effectively the same for each structure. This can be shown to be rigorously true for Mie functions and the maximum variation for Morse functions is 0.003 per cent, at  $a = 6$ .

(ii) As is to be expected from the asymmetry of the potential functions, the changes for compression exceed those for expansion.

(iii) For potentials producing comparable values of  $E_G$ , the Mie potentials give a greater variation with parameter than do the Morse potentials.

For particular interactions, it is clear on physical grounds that minimizing the lattice energy must lead to an  $r_1^*$  less than  $r_0$ , i.e. to a repulsive force between nearest-neighbours in the unstrained crystal. Any compression obviously increases this repulsion while Table 1 shows that, after 2 per cent expansion, the force is still repulsive on this model for most potentials, the exceptions being those few for which  $r_1^*/r_0 > 0.98$ .

For second-neighbour interactions, whose significance has been discussed in some detail by DRECHSLER and LIEPACK,<sup>(13)</sup> the force will be attractive so long as

$$r_1/r_0 > 1/b_2 = \begin{cases} 0.7071 & \text{for face-centred cubic} \\ & \text{crystals,} \\ 0.8660 & \text{for body-centred cubic} \\ & \text{crystals.} \end{cases}$$

For face-centred cubic crystals, Table 1 shows that this limit is attained only for Morse potentials

with  $a \lesssim 3.1$ . Thus even for quite large compressions, second-neighbour interactions should remain attractive. In terms of energy contributions, Fig. 4(a) shows that a nearest-neighbour interaction exceeds that of a second neighbour for  $a > 3.8$  and this effect is reinforced in the contributions to lattice energy since  $M_1/M_2 = 2$  [see Fig. 5(a)]. For Mie potentials, calculations show that  $E(r_1)/E(r_2) > 1$  whenever  $2m+n > 17$  and that  $E_1^s/E_2^s > 1$  whenever  $2m+n > 16$ .

In body-centred cubic crystals, a very different situation prevails. Table 1 shows that for Morse potentials with  $a < 4$ , the second-neighbour interactions will be repulsive and this is also true for some of the Mie potentials. Since third neighbours become repulsive only for  $r_1/r_0 < 1/b_3 = 0.6124$ , interactions from these and further neighbours should be attractive. In terms of energy, calculations of  $E(r_i)$  for  $i = 1, \dots, 5$  show that, with potentials appropriate to ideal crystals, the largest energy is associated with the nearest-neighbour interaction for  $a > 5.1$  or  $3m+n > 29$ , with the second-neighbour interaction for  $5.1 > a > 3.3$  or  $3m+n < 29$ , and with the third neighbour interaction for  $a < 3.3$ . The limit of 3.3 is insensitive to changes in parameter but, as can be seen from Fig. 4(b), the limit at 5.1 is sensitive to such changes, decreasing to about 4.6 for 2.5 per cent lattice expansion. In summary, it appears that for most potentials and most parameter values, the largest energy is in fact associated with a second-neighbour interaction. This of course follows also from Table 1 since  $r_1/r_0$  near 0.87 implies that the second neighbours are separated by about  $r_0$ , where the interaction energy approaches its maximum value of  $E_0$ . For body-centred cubic crystals, the region with  $a < 3.5$  which may be appropriate for the alkali metals (Table 2) shows a further interesting feature. For these relatively flat potentials (see Fig. 1), the nearest-neighbour interaction becomes of opposite sign to the other interactions [Fig. 4(b)] and may be of considerable magnitude. At this stage, as pointed out above, the effect of third neighbours is very significant, particularly in contributions to total lattice energy since  $M_1 : M_2 : M_3 = 8 : 6 : 12$ .

The considerations above point out the considerable errors which can be introduced by a theory based on nearest-neighbour interactions

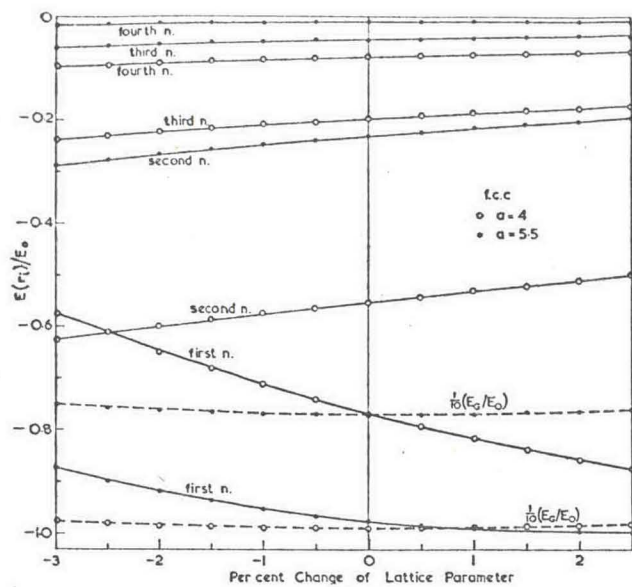


FIG. 3a

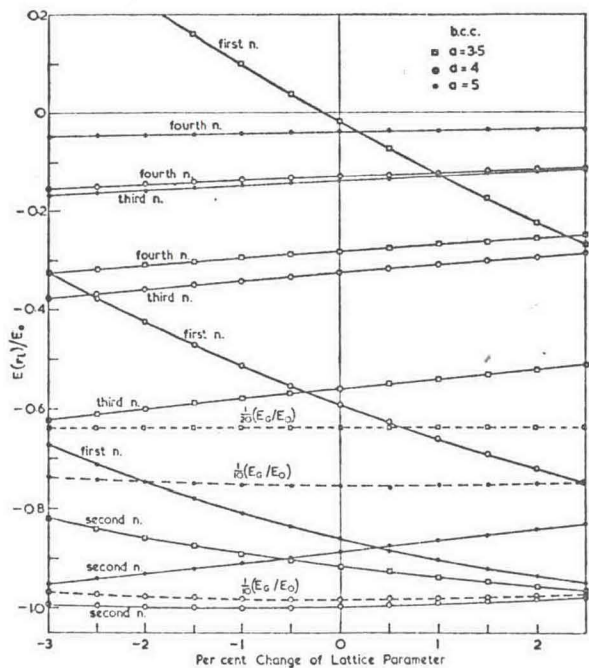


FIG. 3b

FIG. 3. Interaction energy as a function of lattice parameter for various neighbours interacting with Morse potential of (a)  $a = 4$  and  $5.5$ , in a face-centred cubic crystal, and (b)  $a = 3.5$ ,  $4$ , and  $5$ , in a body-centred cubic crystal. The broken lines show a fraction of the total lattice energy.

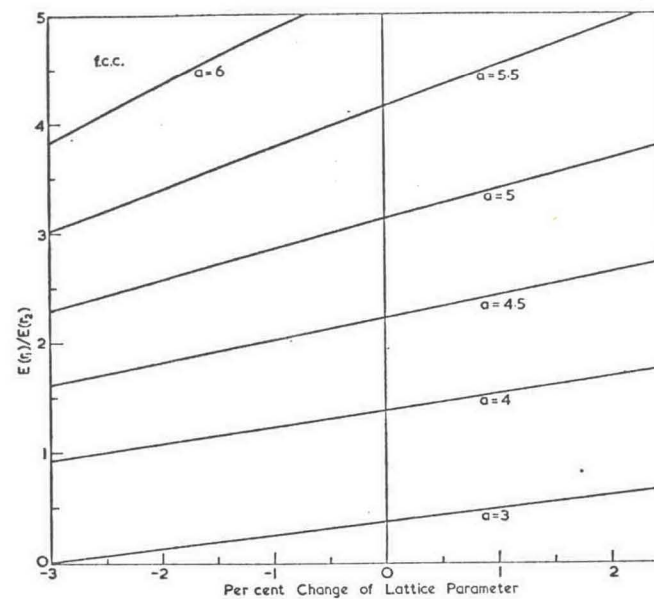


FIG. 4a

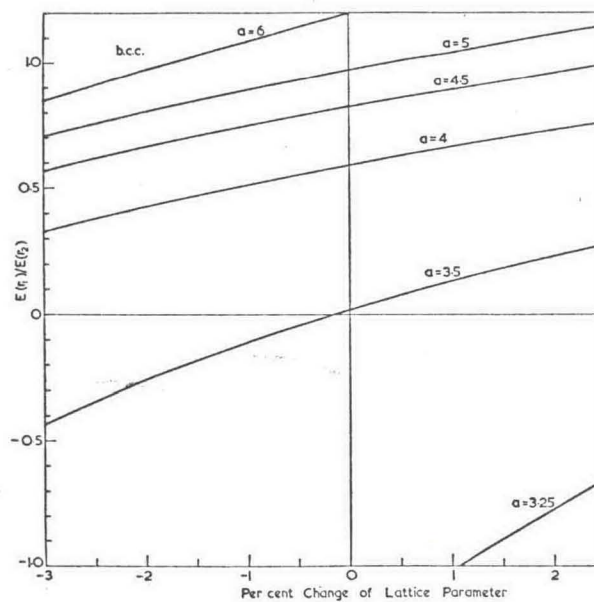


FIG. 4b

FIG. 4. Variation with lattice parameter of  $E(r_1)/E(r_2)$  for various Morse potentials in (a) a face-centred cubic crystal and (b) a body-centred cubic crystal.

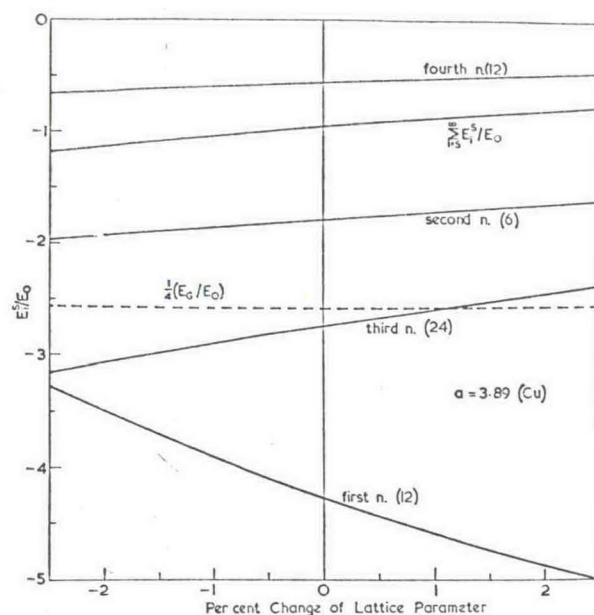


FIG. 5a

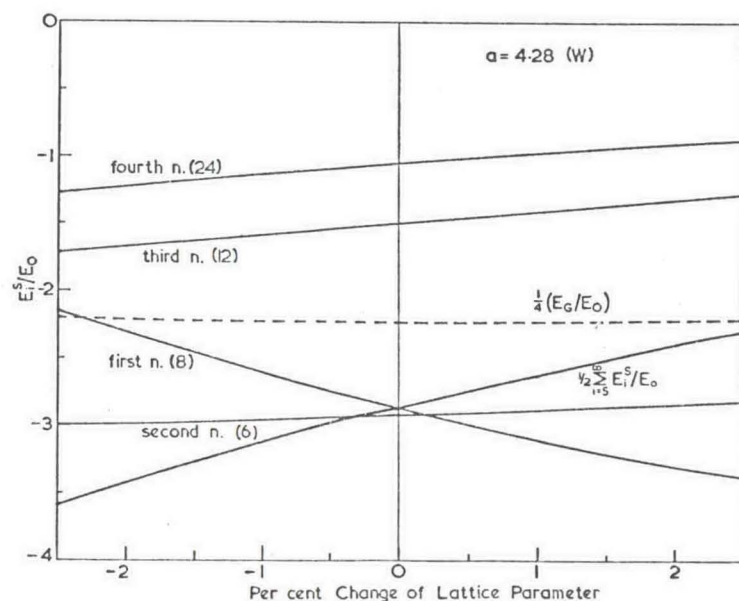


FIG. 5b

FIG. 5. Variations with lattice parameter of various contributions to  $E_G$  in (a) a face-centred cubic crystal for a Morse potential of  $a = 3.89$  and (b) a body-centred cubic crystal for a Morse potential of  $a = 4.28$ ; according to (3) these values are appropriate to Cu and W. The number of atoms in each shell of neighbours is given in brackets.

only, particularly for body-centred cubic crystals. One direct example of this has been pointed out by DRECHSLER and LIEPACK<sup>(13)</sup> in connection with the growth of a (110) face in a body-centred cubic crystal. Here, a single adatom on top of such a face could locate itself on a site with three nearest-neighbours but instead, since growth occurs on such faces, must be located on a site with two nearest and two second-nearest neighbours. This is consistent with detailed calculations with pairwise potentials which show that the latter site has a lower energy.

An interesting demonstration of the effects of distant neighbours has been produced by constructing ball-and-spring models of body-centred and face-centred cubic crystals.<sup>(14)</sup> Conventional models of this type use springs only between nearest neighbours and since these are made identical they are all in equilibrium for an unstrained crystal. However, the new models use springs between atoms up to third-neighbour separation with spring constants adjusted to fit particular interaction potentials. In these, of course, the nearest-neighbour springs are always in compression and the model gives notably different results from the conventional one when used to study the stability of structures, their elastic properties or the positions of surface atoms relative to their ideal lattice positions.

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