



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