(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,[5–8] but did not pursue this investigation for the following reasons:

(i) The only explicit potentials available are those of JOHNSON, HUTCHINSON and MARCH,[7] 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,[9] 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

$$E_G = \tfrac{1}{2}\sum_i M_i E(r_i), \qquad (1)$$

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

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

where

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

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

The potentials considered were either Morse potentials of the form

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

or Mie (Lennard–Jones) potentials of the form

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

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

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

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

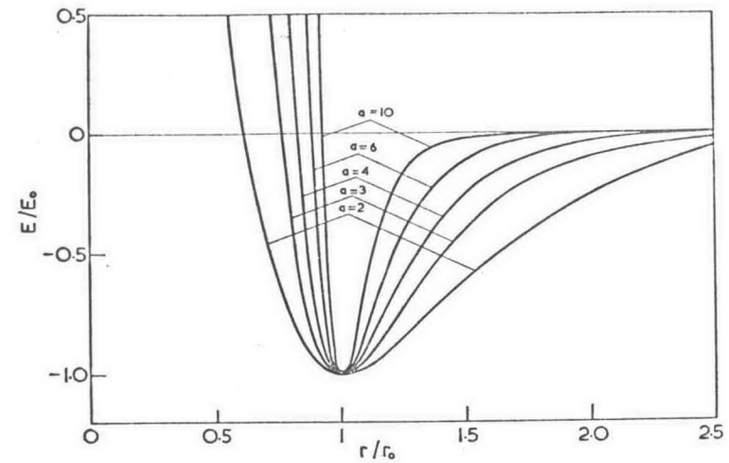

FIG. 1. Morse functions for various values of the Morse constant a.

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

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

where

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

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

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

The lattice sums $S(j)$ have been calculated by JONES and INGHAM[10] 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[3] 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.[2] Some discussion of this appears in Section 4(b) of the following paper.[1]

(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 $\pm 2{\cdot}5$ per cent for the Mie potentials and up to ± 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