Twist-boundary energy in aluminium
An *ab initio* calculation

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Abstract

The variational method of Fletcher and Adamson is used, together with an interaction potential due to Harrison, to calculate the energy of a (100) twist boundary in aluminium as a function of twist angle. The calculated energy rises from a cusped zero for zero misfit to high-angle misfit values of about 500 to 700 erg cm^{-2}, in reasonable agreement with the only experimental data available.

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§ 1. Introduction

Calculations of the energies of grain boundaries in metals have generally been made in terms of the dislocation model introduced by Read and Shockley (1950). This theory is perfectly satisfactory for small misfit angles and, if the elastic moduli of the metal are assumed known, it contains only one adjustable parameter which is related to the core energy of an isolated dislocation. For misfit angles greater than about 15°, however, the physical picture upon which this model is based loses its validity because the dislocation cores begin to overlap, and for angles greater than about 30° the numerical predictions become unreliable.

More recently several other approaches to modelling a crystal interface to examine its behaviour have been developed. A critical review of some of these has been given by Fletcher (1971) while others are described in the Proceedings of the International Conference held at Yorktown Heights in 1971 (Chaudhari and Matthews 1972).

If real interfaces are to be considered in detail, then there seems to be no alternative to a careful calculation using a realistic interatomic potential, and here there are two possibilities : the real-space computer calculations exemplified by the work of Hasson, Boos, Herbeuval, Biscondi and Goux (1972) and of Weins, Gleiter and Chalmers (1971) and Weins (1972), and the reciprocal space variational method introduced by Fletcher and Adamson (1966) and further examined by Lodge (1970).

The real-space calculations give excellent results when applied to tilt boundaries of small repeat distance, using a Morse or similar potential (Hasson *et al.* 1972, Weins 1972). The reciprocal space method is more suited for epitaxial problems and for twist boundaries and again gives useful results when a simple potential is assumed (Fletcher 1967).

The purpose of the present paper is, however, to present an *ab initio* calculation of twist boundary energy for aluminium, using a quantum-mechanically derived interaction potential due to Harrison (1966), in order to evaluate the difficulties involved in such a procedure.

§ 2. BASIS OF THE THEORY

For any grain boundary, the energy problem essentially reduces to finding that atomic configuration which yields the minimum total free energy (or simply the minimum energy if the temperature is well below the melting point). The problem can reasonably be simplified by approximating the crystal material well away from the interface by an elastic continuum and reserving atomic coordinates for the discussion of just a few atomic layers on either side of the interface. These atomic coordinates can then be varied, taking into account the interatomic potentials and using appropriate connections to the assumed elastic continua, until the energy is minimized.

The method used here is essentially as outlined above, with the vital modification that the whole variational problem is treated in reciprocal space using the Fourier transform $v(k)$ of the interatomic potential instead of the direct potential $v(r)$. The detailed procedure and the reasons for its appropriateness are set out by Fletcher and Adamson (1966) while some additional refinements to the elastic problem and minor amendments to second-order terms are given by Lodge (1970) and by Fletcher and Lodge (1975).

In the original formulation of Fletcher and Adamson (1966, eqn. (21)) the elastic strain energy for a half-crystal was written in the simplified form

$$E_e = \sum_{i=1}^{3} \sum_{K}^{+} K\eta_i [C_{Ki}^2 + D_{Ki}^2], \tag{1}$$

where C_{Ki} and D_{Ki} are Fourier components of the distortion and η_i are three 'effective elastic constants'. A more correct expression not only makes these η_i explicit in terms of the shear modulus μ but also includes coupling between the C_{Ki} and D_{Ki} through the Poisson's ratio σ. Assuming isotropic elastic behaviour, the elastic strain energy is given by

$$E_e = \sum_{K}^{+} K\mu \left[C_{K2}^2 + D_{K2}^2 + \frac{4(1-\sigma)}{3-4\sigma}(C_{K1}^2 + D_{K1}^2 + C_{K3}^2 + D_{K3}^2) + \frac{4(1-2\sigma)}{3-4\sigma}(D_{K1}C_{K3} - C_{K1}D_{K3}) \right]. \tag{2}$$

The connection formulae between the distortions in the two half-crystals are also extended from the simplified form (Fletcher and Adamson 1966, eqn. (20))

$$\eta_i F_{Ki} = \eta_i' F_{Ki}', \tag{3}$$

to the explicit and rather more complex relations

$$\mu F_{K2} = \mu' F_{K2}', \tag{4}$$

$$\mu(C_{K3} + D_{K1}) = \frac{\mu'}{3-4\sigma'}(C_{K3}' + D_{K1}'), \tag{5}$$

$$\mu'(C_{K1}' + D_{K3}') = \frac{\mu}{3-4\sigma}(C_{K1} + D_{K3}), \tag{6}$$

$$\mu(C_{K1}-D_{K3})=\frac{\mu'}{3-4\sigma'}(C_{K1}'-D_{K3}'), \quad (7)$$

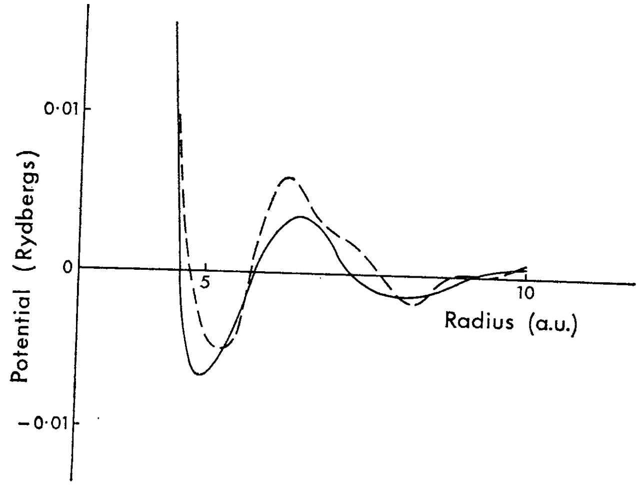
$$\mu'(C_{K3}'-D_{K1}')=\frac{\mu}{3-4\sigma}(C_{K3}-D_{K1}). \quad (8)$$

The meaning of the various symbols is set out by Fletcher and Adamson (1966). These expressions simplify in the present case since $\mu=\mu'$ and $\sigma=\sigma'$.

§ 3. INTERACTION POTENTIAL FOR ALUMINIUM

The effective interaction between atoms in aluminium is built up from two components: the repulsive Coulomb interaction between aluminium ion cores and the shielding effect and mutual interaction of the conduction electrons. This shielding effect is complicated by the sharp decrease to zero of the electron density above the Fermi level, which limits its effectiveness at short wavelengths so that the total interaction resembles an exponentially shielded Coulomb repulsion with, superposed upon it, an oscillation related to the shielding cutoff. This potential, as calculated by Harrison (1966), is shown as the full line in fig. 1. It is the principal minimum produced by the oscillations which is responsible for the net attractive interaction between aluminium atoms in the metal.

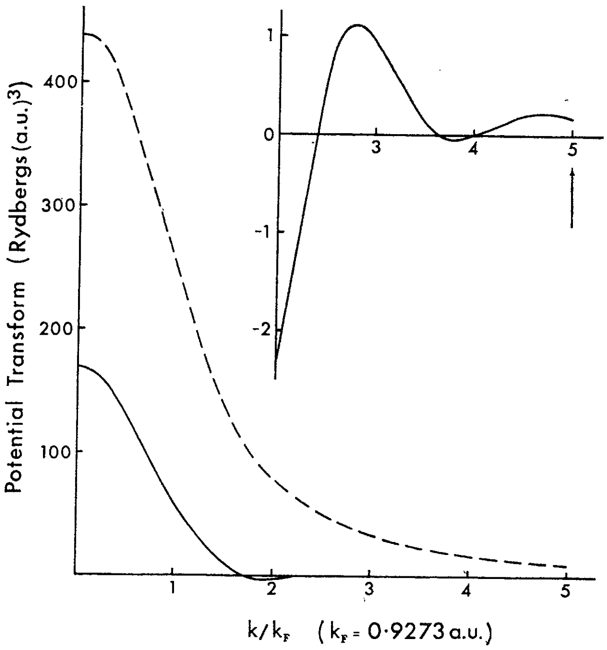
Fig. 1



Effective interatomic potential in aluminium obtained by Harrison (1966) (unbroken line) compared with that obtained from the altered Fourier transform (see fig. 2) truncated at $k=4{\cdot}64$ a.u. (broken line).

At very small distances r the interatomic potential $v(r)$ goes towards infinity like Z^2e^2/r, where Ze is the effective ionic charge. This produces a Fourier transform $v(k)$ which is large and of long range, as shown in fig. 2, and is therefore not very suitable for a variational calculation since components at many reciprocal lattice points are involved. As far as the atomic interaction is concerned, however, the exact form of $v(r)$ at very small r is immaterial, and

Fig. 2



Fourier transform of the effective interatomic potential obtained by Harrison (1966) (broken line) compared with that obtained using the modified core potential (eqn. (9)) (unbroken line and insert). The truncation point of 4·64 a.u. is indicated by the arrow.

the potential can be modified in this region to optimize the form of the Fourier transform. Therefore, a modified core potential (unshielded) is selected, of the form

$$
\begin{aligned}
v'(r) &= \frac{Z^2e^2}{R}\left(2-\frac{r}{R}\right), \quad r<R \\
&= \frac{Z^2e^2}{r} \qquad\qquad\quad, \quad r>R,
\end{aligned}
\tag{9}
$$

where R is chosen small enough (actually 3·5 at. units or about 1·9 Å) that ion overlap into the altered region never occurs. The contribution from the conduction electrons is left the same as before and the resulting form of the transform $v(k)$ is shown as the full curve in fig. 2. The reduction in the range of $v(k)$ is easily apparent.

This potential of Harrison has the advantage from the present point of view of having been derived entirely *ab initio*. It therefore has certain complexities associated with it which are real but which would not appear in a simple model potential like that of Fletcher (1967) after adjustment to fit the physical data for aluminium. One of the best tests of an interatomic potential is to apply it to the calculation of elastic moduli. In the present case the relevant moduli, both for the testing of Harrison's potential and for subsequent use, are those involving no volume change. These elastic moduli c_{ij} as calculated and as found from experiment are shown in the table. For a homogeneous isotropic medium, the shear modulus μ is given by

$$\mu = c_{44} = \tfrac{1}{2}(c_{11} - c_{12}). \tag{10}$$

Elastic constants for aluminium
(c_{ij} and μ in units of 10^{11} dyne cm^{-2}).

	Theory (Harrison)	Experiment
c_{44}	1·5	2·8
$\frac{1}{2}(c_{11}-c_{12})$	3·4	2·3
μ	2·5	2·6
σ	(<0)	0·345

It is evident from the experimental data in the table that aluminium is not completely isotropic, in the sense of the equality required by (10), but that the experimental value of μ for polycrystalline aluminium is equal to the mean of c_{44} and $\frac{1}{2}(c_{11}-c_{12})$. The theoretical values exaggerate the anisotropy but again the mean value, which must be used in the simplified theory, is very close to the experimental value.

Harrison's theory applies essentially to atomic displacements in which the volume of the crystal remains unaltered. Because the potential function omits terms depending upon volume changes it is thus unable to give a good account of elastic quantities like the bulk modulus and Poisson's ratio. For this reason it is not necessary to take too seriously the failure of the theory to predict a physically reasonable value for Poisson's ratio. The values of μ and σ used for the calculation are the experimental values in the table.

§ 4. TWIST BOUNDARY ENERGY

The variational theory is best adapted to the calculation of the energy of twist boundaries on low-index planes. Indeed it was originally developed to treat problems of epitaxial growth where this is the situation of interest. While tilt boundaries can be encompassed by the theory, they are not nearly so simply dealt with. For this reason a calculation of the energy of a twist boundary lying on a (100) plane in aluminium was undertaken.

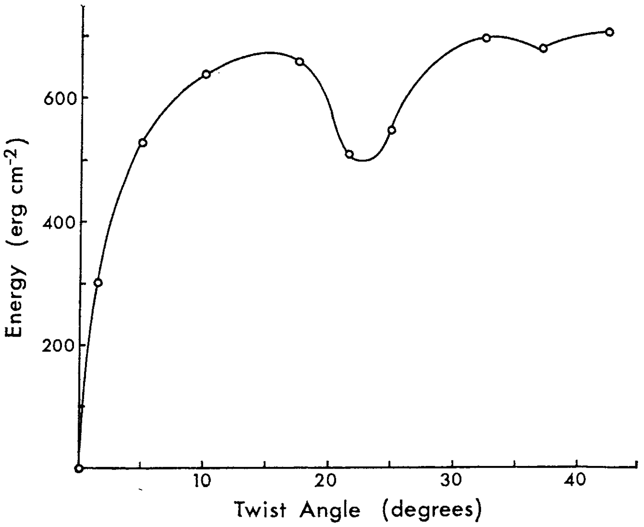
The variational procedure was carried out using the Harrison potential, treated as discussed above, for the interaction between one atomic plane on either side of the interface, the distortion energy for each semi-infinite crystal being taken into account by the elastic continuum approximation. Such a procedure is reasonable for twist boundaries but would not generally be satisfactory for tilt boundaries.

The reciprocal space summation involved in the calculation of the interaction energy (Fletcher and Adamson 1966, eqn. (19)) must be truncated at some appropriate point. This is equivalent to truncating the transform $v(k)$, the effect of which may be seen by determining the potential resulting from the truncated transform. A reasonable value for truncation was taken to be $k = 4{\cdot}64$ a.u. and the potential resulting is shown as the broken line in fig. 1.

The reciprocal space summation parallel to the interface may be further truncated as this simply involves the neglect of certain distortion components. The value used for this truncation was 2·7 a.u. such that the neglected distortion components have a negligible effect on the grain boundary energy. In the same way only distortion components with vectors K of magnitude less than 0·81 a.u. were found to contribute appreciably to the energy.

Even with these simplifications the computational problem is long because of the number of variational parameters and the complexity of the second-order terms. Computation for a single twist orientation took up to 2 hours on an ICL 1904–A computer. For this reason only ten points were calculated, as shown in fig. 3. With the exception of the point for zero misfit, which is accurate and provides a base energy for the other points, the calculation gives an upper bound as well as a first approximation to the grain boundary energy.

Fig. 3



Calculated grain boundary energy as a function of angle for a twist boundary lying on a (100) plane in aluminium.

The calculated behaviour is, however, in reasonable agreement with expectations. There is a cusped energy minimum at zero misfit, and the grain boundary energy rises to between 500 and 700 erg cm^{-2} for high-angle misfit. The only coincidence boundary for which there is evidence of a cusp is for the 2, 1→1, 2 coincidence at 36° 52·2′. The large minimum at about 22° arises from the combined effects of the distortion vectors joining the surface reciprocal lattice points 1, 0→1, 0 ; 1, 1→1, 0 ; 0, 1→1, 1 ; 1, 1→1, 1 ; 2, 1→2, 0 in the first quadrant and the corresponding vectors in the other three quadrants. There is also a minimum in the interplanar spacing across the interface in the same region. Although the minimum appears to coincide with a coincidence boundary at 22° 37·2′, the corresponding coincidence in the surface reciprocal lattices (3, 2→2, 3) is outside the range of the truncated potential transform and so will not affect the energy. The curve is symmetrical about 45° misfit through the symmetry of the theory. The value of the large-angle grain boundary energy is in satisfactory agreement with the result 630 ± 100 erg cm^{-2} found calorimetrically by Astrom (1957).

Details of the calculation are, however, somewhat less satisfactory. The interplanar spacing across the interface for zero twist angle is about 8% smaller than the proper (100) spacing in aluminium, corresponding to a nearest neighbour distance 4% too small and suggesting a shortcoming in the potential itself. This potential is determined from the band structure energy of a perfect lattice and may not well represent the potential seen by atoms in a distorted lattice. More serious, perhaps, is the restriction of the interaction across the interface to only one atomic plane on either side.

The truncation of the transform $v(k)$ also introduces an error in the calculations. Comparison of the two potentials in fig. 1 suggests that an error of 20% could be introduced in a real space energy calculation. The effect on the reciprocal space calculation is expected to be similar. This is corroborated by the effect of the truncation on integral approximations to the surface reciprocal lattice summations involved, which have about the same error. The total effect is, however, a little more subtle than this.

In plotting the grain boundary energy of fig. 3, the zero of energy was taken at zero misfit by convention. This in fact corresponded to a calculated interaction energy of -698 erg cm^{-2}. The error in the zero misfit energy due to truncation is thus about ± 150 erg cm^{-2}. For high-angle misfits the 20% error occurs in interaction energy dependent coefficients of the various distortion components. As no large cancellation is involved in these terms an error not greatly larger than 20% is to be expected. The interaction energy for high-angle misfits being on average about -200 erg cm^{-2} this gives an error of ± 50 erg cm^{-2} in this region.

It is concluded, therefore, that a calculation of the twist boundary energy from first principles is feasible using the reciprocal-space variational method. The calculation time, is however, rather long and a method using an appropriately chosen model potential may be of more practical utility.

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