PHYSICAL REVIEW B VOLUME 60, NUMBER 4 15 JULY 1999-II

Computer simulation of general grain boundaries in rocksalt oxides

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(Received 29 January 1999; revised manuscript received 26 March 1999)

The structures and energies of a series of tilt grain boundaries and corresponding surfaces were calculated to obtain a general relationship between the grain boundary energy and the tilt angle for NiO and MgO. We show that the simple elastic expressions for the grain boundary energy give reasonable results for low-angle grain boundaries. We investigate the assumptions that lie behind thermal grooving experiments and show that the torque terms should be large, even when far from a major pole [the (100), (110), or (111) directions]. However, the measured angles agree better with the calculations when torque terms are ignored. We discuss this effect in terms of faceting and oxidation of the surface. [S0163-1829(99)06627-8]

I. INTRODUCTION

Most materials have a polycrystalline structure with grain boundaries at the point where two crystallites meet. These boundaries are often complex structures. In principle, they are defined by the mutual orientation of the crystallites but may have a complex structure of their own and may also contain large amounts of impurity. This often produces a boundary region with a distinct phase—the interphase. There are, however, two special cases of boundaries on which most experiments and calculations have been done—the tilt (and to a lesser extent the twist) boundaries. These are distinguished by the manner of their construction. If the two crystallites are rotated with respect to each other about an axis perpendicular to the interface between them, then the boundary is called a twist boundary whilst if the axis of rotation is parallel to the interface then the boundary is called a tilt boundary. Although extensive work on simulating grain boundaries within metals using pair potentials has been carried out,[1] there is comparatively little work on the simulation of boundaries in ionic materials. Duffy and Tasker studied grain boundaries in NiO.[5] Subsequent work has only considered boundaries with high coincidence and which contained either a pure twist or tilt boundary. Low-angle grain boundaries present particular difficulties because of the large surface unit cells required. The energies of these boundaries (in metals) have been obtained by treating them as a wall of dislocations and using simple elastic theory. Read and Shockley[2] showed that the energy per unit length of a grain boundary is given by an expression of the form

$$E(\theta)=E^0\,\theta(A-\ln\theta), \tag{1}$$

where E^0 and A are constants. E^0 contains information about the elastic properties of the bulk whereas A contains information about dislocation cores. Wolf[3] showed empirically that the expression

$$E(\theta)=E^0\sin\theta[A-\ln(\sin\theta)] \tag{2}$$

gave a better fit to calculations on metal grain boundaries. Further details can be found in Ref. 4.

There are no direct measurements on grain boundary energies. Some information can be obtained from thermal grooving experiments (sometimes called thermal etching.) Within a material most grain boundaries meet in sets of three at a triple point. However, grooves form at the points where a boundary meets the surface when the material is heated. By measuring the dihedral angle, Ψ, of this groove and ignoring the torsional components of the energy, the ratio of boundary to surface energy (γ_b/γ_s) is given by

$$\gamma_b/\gamma_s=2\cos(\Psi/2). \tag{3}$$

A diagram of the configuration of the experiment is given in Fig. 1. Thermal grooving experiments have been carried out on NiO by Dhalenne *et al.*[6,7] who showed that the groove angle [presented in their work as γ_b/γ_s using Eq. (3)] varied as a function of the orientation angle of a twin boundary and included cusps at the angles that corresponded to special boundaries (i.e., low-index boundaries with high coincidence). However, there was some disagreement between these results and the calculations of Duffy and Tasker.[8] One of the aims of this paper is to study this inconsistency.

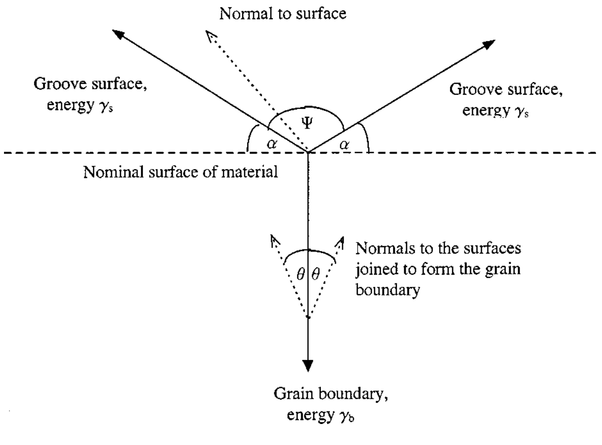

FIG. 1. Angles defined for the thermal grooving experiment.

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TABLE I. Potential parameters used in the calculation. Details are given in Refs. 10 and 11. Distances are in Å and energies in eV. The short-range cutoff was $1.6a_0$ where a_0 is the nearest-neighbor cation-anion distance.

Magnesium oxide: Short-range interactions			
Interaction	A (eV)	ρ (Å)	C (eVÅ^6)
Mg^{2+}–O^{2-}	1275.2	0.3012	
O^{2-}–O^{2-}	22764.3	0.149	20.37
Magnesium oxide: shell model			
Ion	Ion charge ($\|e\|$)	Shell charge ($\|e\|$)	Spring constant (eVÅ^2)
Mg^{2+}	+2.0	0.0	Rigid ion
O^{2-}	−2.0	−2.8107	46.126
Nickel oxide: Short-range interactions			
Interaction	A (eV)	ρ (Å)	C (eVÅ^6)
Ni^{2+}–O^{2-}	1582.5	0.2882	
O^{2-}–O^{2-}	22764.3	0.149	27.88
Nickel oxide: shell model			
Ion	Ion charge ($\|e\|$)	Shell charge ($\|e\|$)	Spring constant (eVÅ^2)
Ni^{2+}	+2.0	3.344	93.7
O^{2-}	−2.0	−3.0	54.8

II. THE CALCULATION

Since we wish to perform a large number of calculations on up to several thousand ions, we have used a classical simulation method based on central-force pair potentials and a shell model. Full ionic charges are used; the short-range interaction takes the form

$$V(r)=A\exp(-r/\rho)-C/r^6, \tag{4}$$

where the parameters A, ρ, C can either be fitted to suitable experimental data or calculated using a variety of approximations. The electronic polarizability of the ions (except for Mg^{2+} which is treated as a rigid ion) is included using the shell model of Dick and Overhauser.[9] In this model, the ions are treated as massless cores linked to massless shells by a spring. The coulombic terms act between all species (except for cores and shells of the same ion); the short-range terms act between the shells only. For convenience, the parameters used are collected in Table I. Details of their derivation are given in Refs. 10 and 11. In recent years, a number of comparisons for both bulk and surface structures have been made between models of this kind and quantum-mechanical calculations of various kinds. In particular, for MgO, both Hartree-Fock calculations and calculations based on the local-density approximation have been performed on the (001) surface and compared with classical shell models.[12] These show excellent agreement between the methods for the surface energies. The calculations disagree on the sign of the small amount of rumpling observed; the Hartree-Fock calculation obtaining the opposite sign to the other two. Unfortunately this issue has not yet been resolved by experiment; the accuracy is not sufficiently great. There is no comparison possible with NiO because the only reported calculations of the surface of NiO are local density calculations. It is well-known that such calculations encounter very considerable problems in giving an adequate description even of bulk nickel oxide. The most accurate recent work[13] (which is still compelled to include the Mott-Hubbard correlation terms in an empirical fashion) discusses the electronic surface states but not the structure or the surface energy (where a comparison with classical simulations would be possible). The only comparison of grain boundaries in the literature is that of Ref. 14 on the twist grain boundary of MgO. Here the agreement between the classical and electronic structure calculation is excellent. The overall comparison of electronic structure calculations of the surfaces with ionic crystals with classical simulations (see Ref. 15 for references to other comparisons) suggests that the classical methods are well able to describe a wide range of interfaces in ionic systems.

We need to simulate a large set of tilt grain boundaries and their corresponding surfaces. The various classical simulation codes developed to do this use a common strategy pioneered by Tasker.[16] The crystal is considered as a stack of planes normal to the interface to be calculated. (In the case of an asymmetric tilt boundary, we will need to define two separate stacks of planes that meet at the interface). Periodic boundary conditions are imposed in the plane of the interface, but not in the direction perpendicular to it. The calculation of the coulombic terms for such an arrangement are well known; the first discussion is that of Parry.[17] The two-dimensional summation is performed within the plane and these planes are then summed in the perpendicular direction. The stack is divided into two regions; an inner region containing the interface and two outer regions beyond on either side of the interface. The ions in the inner region are relaxed to positions of zero force using either a standard Newton-Raphson method or (for the largest calculations) a conjugate gradient technique. The ions in the outer regions are fixed relative to each other, but the regions are allowed to move to allow dilatation of the boundary. The choice of the boundary between the regions is chosen so that increasing the size of

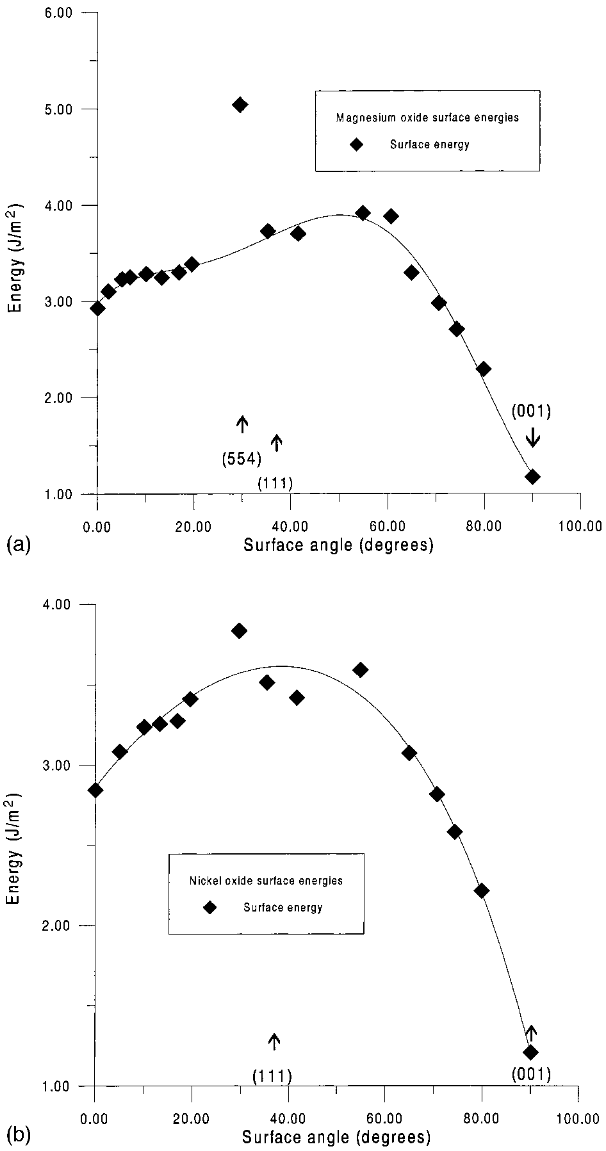

FIG. 2. Surface energies as a function of angle with respect to (110) for MgO (a) and NiO(b).

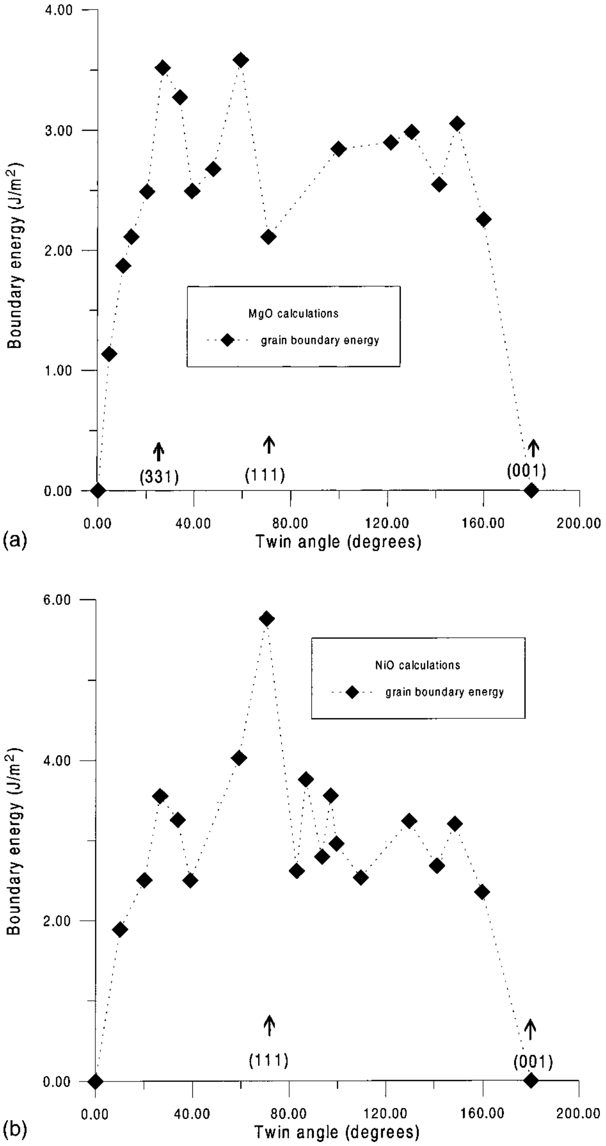

FIG. 3. Grain boundary energies as a function of twin angle (twice the tilt angle) for MgO (a) and NiO(b).

the inner region further does not affect the results (i.e., all the short-range relaxations due to the presence of the interface die away before the boundary is reached). In practice, this means that the inner region is 30–40 Å thick depending on the surface under discussion. The number of ions in the inner region varies, being greatest for the vicinal surfaces (since these have the largest surface unit cells). In this case, there may be 5000 ions in the inner region. The METADISE code[18] was used for the simulations.

III. RESULTS

We first consider the surface energies and grain boundary energies. These are given in Figs. 2–4. In some of the calculations, it was clear that the system had reached only a local, rather than global minimum. These calculations were discarded. The curves in Fig. 2 are fits to fifth-order polynomials. Such functions can represent the general shape of the curve, but not the details of the faceting. Clearly, it would be possible to make a curve pass through all the calculated points by using a cubic spline, but this would still involve us in assumptions about the shape of the surface energy curve between those points. The important point is that the shape of the curve is different from the analogous curves for metals. There is no flat region away from the major poles [i.e., such directions as (100), (110), and (111)]. Moreover, since the surface energies of the (110) and (100) directions are so different (by 2.7 J/m^2) there must be an overall downward slope as a function of surface angle from (110) to (100) This is important when we consider the torque terms.

There are two ways of expressing the energy of a grain boundary; the first (Fig. 3) is with respect to the perfect lattice (and is usually called the grain boundary energy); the second (Fig. 4) is with respect to the surfaces out of which the boundary is constructed (and is usually called the binding energy). The first definition is our main concern here. MgO and NiO have similar (but not identical) curves for the boundary and binding energies as a function of the twin angle (the angle between the normals to the two nominal surfaces that are joined to make the boundary).

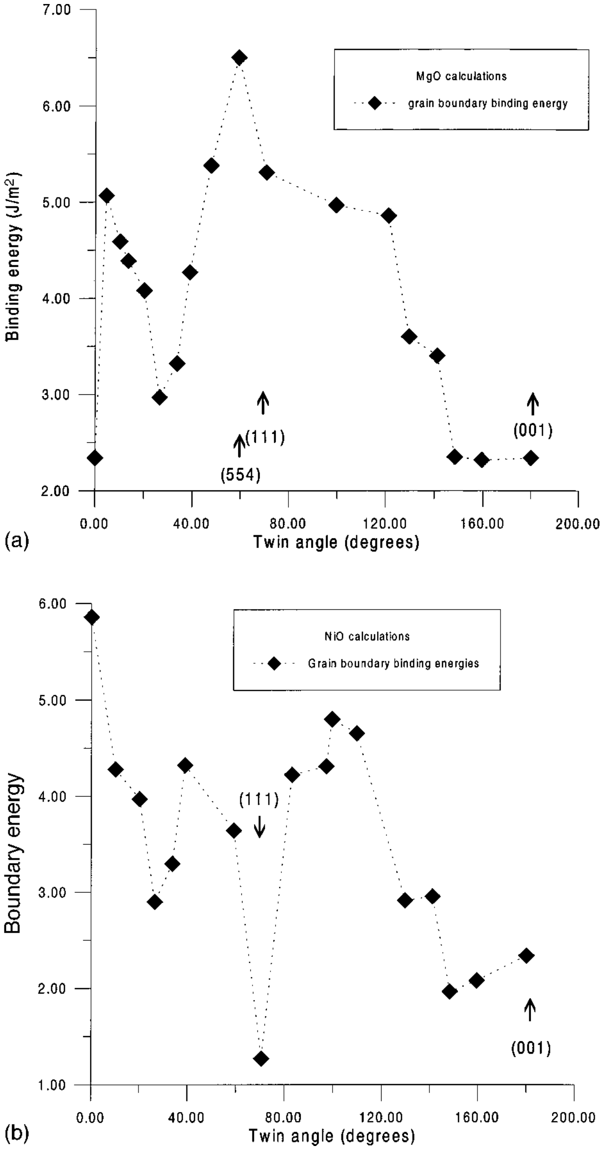

FIG. 4. Binding energies of the grain boundaries as a function of twin angle for MgO (a) and NiO(b).

We first consider the connection between grain boundary energy and grain boundary structure. As can be seen from Fig. 5, the boundaries consist of a series of small channels formed by the step structure of the interface. For high-angle boundaries, for example the (331) boundary, these channels are very close together. As the boundary angle decreases these channels move further apart from each other. Beyond a certain angle the dislocation cores begin to retain the same structure although the distance between them increases. Thus, for very low-angle grain boundaries, the structure can be thought of as a series of edge dislocations as described by the dislocation model.[2] However, as the angle of the boundary increases these dislocation cores overlap and become hard to distinguish. It is possible to fit the low-angle boundaries to the expressions 1 and 2 discussed above. The results are shown in Table II. The value of E_0 can be estimated from the elastic properties of the material;[4]

$$E_0 = \frac{\mu b}{4\pi(1-\nu)}, \tag{5}$$

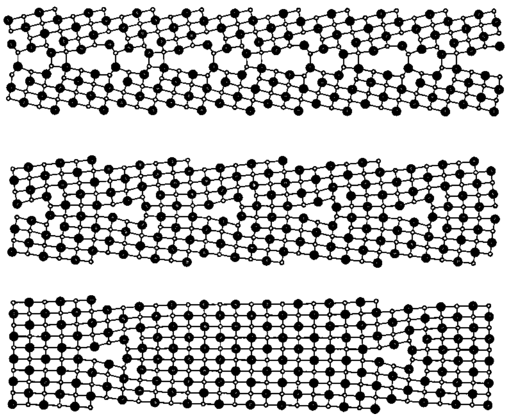

FIG. 5. Structure of grain boundaries from high to low tilt angles (331) (top), (661) (middle), (18181) (bottom).

where μ is one of the Lamé constants, ν is Poisson's ratio, and b is the magnitude of the Burger's vector of the dislocations forming the boundary. For both MgO and NiO this gives a value for E_0 of about 5.3 J/m^2. The fitted values are reasonably close to this given the simplicity of the theory. The value of A is more difficult to estimate since it requires knowledge of the dislocation core energy. This can be obtained but we have not attempted it here.

The parameters of the two expressions are similar. This is to be expected since $\sin\theta \approx \theta$ for low-angle boundaries. The advantage of the Wolf expression in metals is that it gives a reasonable representation of the grain boundary energy across the entire range of angles. It can be seen from the parameters in the table that this is unlikely to be true for ceramics. For MgO, the A parameter is *negative*. This can produce a reasonable fit for small angles (where the second term is positive) but not for large angles. The parameter values for the boundaries with respect to (110) and (100) are quite different, as might be expected from the graph of the energies (Fig. 3).

We now proceed to calculate the grooving angle as follows. We first ignore the torque terms. Thus, we take a given twin grain boundary and solve the equation

$$\gamma_b = 2\gamma_s(\Psi)\cos(\Psi/2). \tag{6}$$

Provided that the groove is entirely symmetric (i.e., the same surfaces on both sides and the grain boundary perpendicular to the overall surface of the specimen), we have a simple relation between the groove angle Ψ and the angle of the surface of the groove (α) with respect to the overall surface [assumed to be (110)]: $\Psi = \pi - 2\alpha$. This angle is plotted as a function of boundary twin angle (θ) in Fig. 6 (see Fig. 1 for nomenclature), together with the experimental data of Dhalenne *et al.*[6,7] A number of points should be noted. First, since it is our purpose to investigate the size of the torque term, we have reconverted the experimental results back to groove angles using Eq. 3. The results in Fig. 6(b) show that there is a good match between the shapes of the experimental and calculated curves, with a series of cusps in the energies that correspond to those boundaries that have previously been simulated. One particularly deep cusp at 70.53° is due to the (111) boundary which, as Duffy and Tasker[8] pointed out, is a coherent twin. However, there is a significant dis-

TABLE II. Parameters E^0 (J/m^2) and A for the Read [Eq. (1)] and Wolf [Eq. (2)] expressions for low angle boundaries in MgO and NiO. The directions [(110) and (100)] gives the major pole with respect to which they are low-angle boundaries.

	MgO (110)		MgO (100)		NiO (110)		NiO (100)	
	E^0	A	E^0	A	E^0	A	E^0	A
Read	9.41	−0.24	6.08	0.25	6.31	0.56	5.96	0.36
Wolf	9.41	−0.23	6.13	0.25	6.31	0.58	6.00	0.36

crepancy between the experimental and calculated angles in the region $120° < \theta < 140°$. It is true that one of the experimental points has a very large error bar, but even so, this is not enough to resolve the problem.

One possibility is that the torsional terms that we have neglected are important. These are given in the full expression for the equilibrium of three boundaries at a point[19,20]

$$\sum_{i=1}^{3} \gamma_i \mathbf{t}_i + \left(\frac{\partial \gamma_i}{\partial \psi_i} \right) \mathbf{n}_i = 0. \tag{7}$$

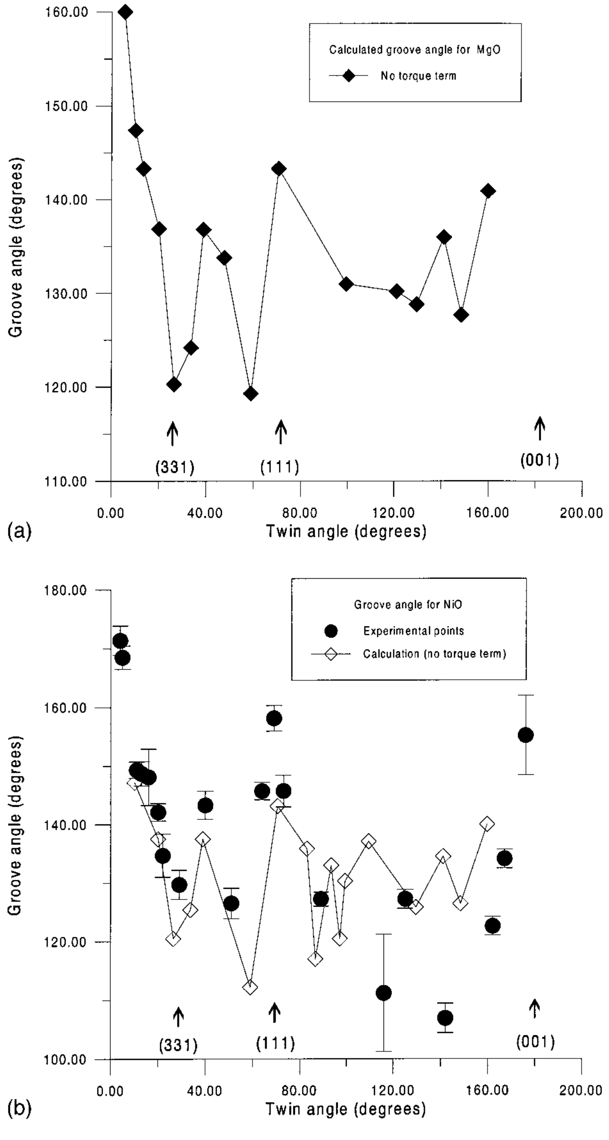

FIG. 6. Calculation of the groove angle ignoring the torque terms for MgO (a) and NiO (b). Experiments for NiO from Refs. 6 and 7.

γ_i is the energy of a boundary defined by a vector $\mathbf{t}_i$ in the plane of that boundary and normal to the line of intersection of the three boundaries. $\mathbf{l}$ is a unit vector along that intersection line and $\mathbf{n}_i = \mathbf{l} \times \mathbf{t}_i$. ψ_i is the angle between boundary i and the next boundary clockwise around the intersection line. In the case of a twin boundary perpendicular to the surface, matters are considerably simplified. We can ignore the torsional effect of the grain boundary (provided that the boundary is close to perpendicular to the surface). This gives as our force balance equation

$$\gamma_g = 2\gamma_s \cos(\Psi/2) - 2\left(\frac{\partial \gamma_s}{\partial \alpha} \right) \sin(\Psi/2), \tag{8}$$

where we can identify the angle α as the misorientation of the plane of the groove with respect to the overall surface plane (see Ref. 21). We, therefore, obtain the surface torsional term from the plot of the surface energy as a function of groove angle using the relation $\Psi = \pi - 2\alpha$ (the angles are as in Fig. 1). Our revised expression for the groove angle is

$$\gamma_b = 2\gamma_s(\Psi)\cos(\Psi/2) + 4\left(\frac{\partial \gamma_s(\Psi)}{\partial \Psi} \right) \sin(\Psi/2). \tag{9}$$

The second term can be calculated provided that we assume that our approximation of the angle dependence of the surface energy by a polynomial is reasonable. The results are shown in Fig. 7. From this it is clear that the torque term does have a large effect, but that it worsens rather improves agreement with experiment. The reason for the large torque term can be seen from Fig. 2; the surface energy varies strongly with angle for the angles in the region of the calculated (and experimental) groove angles. This is quite different from the behavior observed for metals by Hodgson and Mykura,[21] where the surface energy varied strongly with angle only in the region of the poles.

One interesting feature of the calculation is the variation of the surface energy as a function of the boundary twin angle. This is shown in Fig. 8. In all cases (except for low-angle boundaries) the spread of values of the surface energy is low (about ±0.1 J/m^2 at most.) As far as the first term is concerned, the surface energy could be approximated by a constant and the shape of the groove angle curve would reflect the shape of the grain boundary energy since the torsion term would be zero. This illustrates a critical assumption that we have made; that we can identify the surface at a given groove angle with the perfect surface appropriate to that angle. There are two reasons why that might not be so. First there is the possibility of faceting. As an extreme example, there is a peak in the surface energy for the (554) surface [Fig. 2(a)]. This is also revealed in the plot of the binding energy of the boundaries (the stability of the boundary with

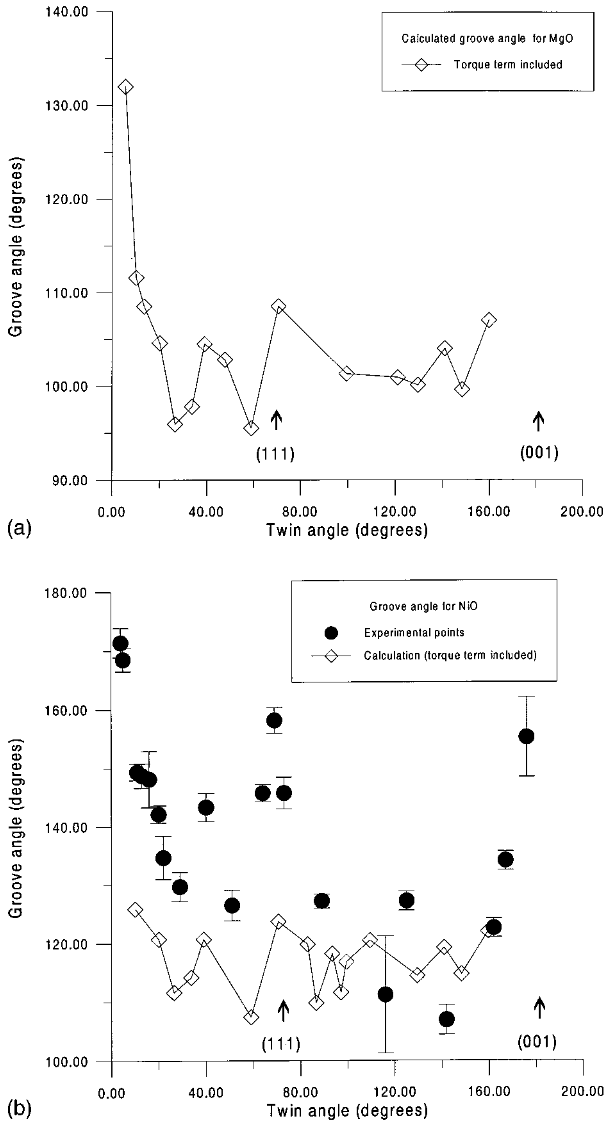

FIG. 7. Calculation of the groove angle including the torque terms for MgO (a) and NiO (b). Experiments for NiO from Refs. 6 and 7.

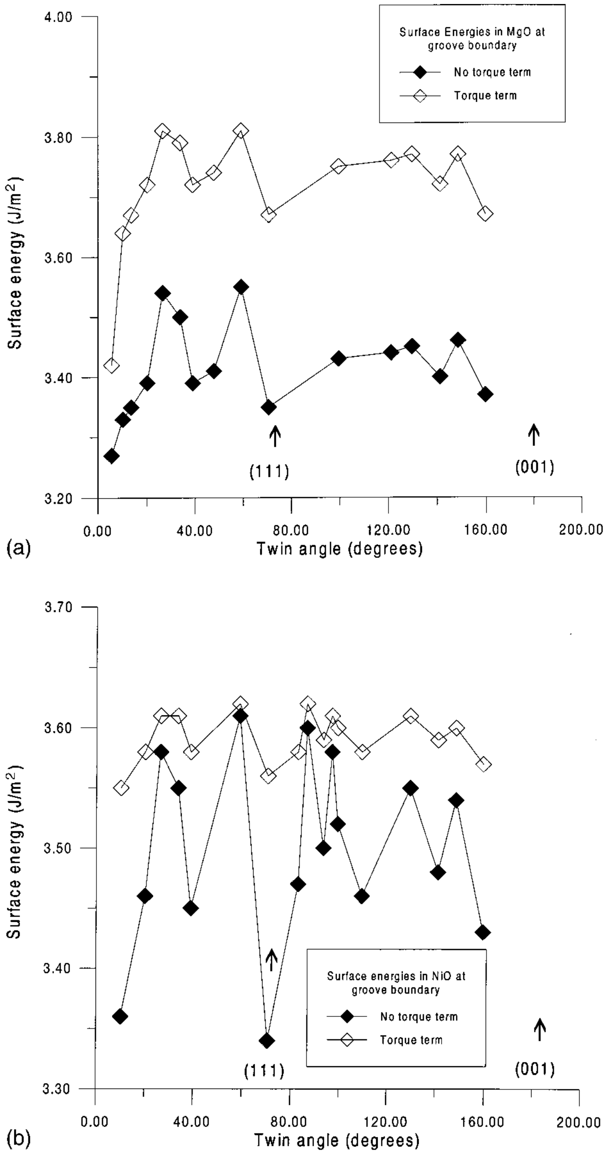

FIG. 8. Calculated surface energies appropriate to the grooves for various boundary twin angles: MgO (a) and NiO (b).

respect to forming two free surfaces) as shown in Fig. 4(a). The energy is very high relative to the other energies of the neighboring surfaces and may be a result of using the standard method of restructuring to quench the dipole associated with this surface. Work by de Leeuw *et al.*[22] has shown that faceting is a favorable process on some surfaces. For example, faceting of the (110) surface of MgO lowered the surface energy from 3.02 to 1.87 Jm^{-2}. Faceting of the (554) surface resulted in a lower energy of 3.26 Jm^{-2}, similar to that calculated for the unfaceted (111) surface. However, this cannot remove our problem; the surface energy curve for angles close to the groove angle decreases monotonically and there is no obvious way that faceting can alter this. Indeed, it is likely that by fitting the surface energy to a smooth function we are (in effect) assuming some degree of faceting. This is clear from Fig. 2(a) where the requirement to fit to a reasonably simple function has, in effect, discarded the (554) surface from consideration. The second possibility is a change in the effective surface energy due to the formation of surface defects. This is possible in nickel oxide. It readily oxidizes, particularly at high temperature. The experimental procedure is not discussed in sufficient detail to determine how likely this is. Calculations by Oliver[23] show strong variation of the surface energy as a function of oxidation. The effect is different for different boundaries; the surface energy of the (100) and (110) boundaries rises, whereas the energy of the (111) boundary falls. It is likely that the effects of oxidation would smooth out the variation of surface energy with angle. A quite different possibility is that the assumption that the grain boundary is perpendicular to the surface is incorrect. If the boundary was more than about 5° degrees away from perpendicular, the grain boundary torque term would begin to become significant. There is no indication from the experiments that this is so.

IV. CONCLUSIONS

We have used atomistic simulation to calculate the grain boundary energy and structure for oxides of the rock salt structure. The energies and structures of the low-angle boundaries are what we would expect from a simple dislocation model. We have attempted to compare the calculations of the energies with the thermal grooving experiments of Dhalenne and co-workers.[6] Here, there are a number of problems. First, if we interpret the experiment in the obvious manner, with the grain boundary perpendicular to the overall surface and the groove boundaries being the relevant pure surfaces, then agreement between the calculations and experiment is poor. Furthermore, if this analysis of the experimental situation is correct, the assumption made in the experimental analysis, that the torque terms can be ignored, must be incorrect. Although it is usually the case that the torque terms are negligible in metals, the calculations show that this is a very dangerous assumption to make in ceramics. The only way that the experiments and calculations can be (at least partially) reconciled is to assume that the surfaces of the grooves are not the pure surfaces corresponding to the angle of the groove, but can be described by an average surface energy of about 3.4 J/m^2. If true, this suggests that, in this case at least, the groove angle directly monitors the grain boundary energy. It is unfortunate that almost no information on thermal grooving is available on any system other than nickel oxide. This is particularly the case since such experiments are almost the only way of obtaining information on boundary energies rather than boundary structures. More experimental information on other systems is highly desirable to investigate the issues discussed here.

ACKNOWLEDGMENTS

The authors would like to thank Dr. G. W. Watson for useful discussions during the initial phase of this work. The calculations were performed on the T3D and T3E computers at Edinburgh as part of the Materials Science Consortium supported by EPSRC. D.J.H. thanks the N.E.R.C for financial support and M.S.I. for the use of its INSIGHT II program.

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