

## Conductivity and ‘negative $U$ ’ for ionic grain boundaries

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**Abstract.** We show that charge-transfer excitations (like  $2M^{2+} \rightarrow M^+ + M^{3+}$ ) can be lowered greatly in energy near grain boundaries, where sites are no longer equivalent. In special cases the excitations may be exothermic (‘negative- $U$ ’ behaviour); likely cases include (320) and (122) grain boundaries in FeO. Consequences include effects on conductivity, segregation of impurities with different valence, and on other charge-state-dependent properties.

### 1. Introduction

The phenomena we discuss relate to the electrical and optical behaviour of polycrystalline materials containing ions which can exist in more than one charge state. Examples would include transition-metal oxides containing grain boundaries. We shall show that, near surfaces or grain boundaries, there can be charge-transfer transitions with a very low energy. These might be excitations such as



which have been discussed as possible descriptions of the lowest band-to-band transitions in oxides (Catlow and Muxworthy 1978). In extreme cases, reaction (1) might be exothermic. This would correspond to the so-called ‘negative- $U$ ’ behaviour (for a discussion for relevant systems and earlier references, see Stoneham and Sangster (1982)).

The consequences of a low energy for reaction (1) are varied. First, there will be conduction (whether by electrons or holes, whether small or large polaron) with low activation energy associated with the grain boundary or surface. Grain boundary conduction will be enhanced, just like the well known enhancement of ionic diffusion reviewed by Atkinson and Taylor (1981). Secondly, there will be distinctive optical absorption at relatively long wavelengths. Thirdly, there may be an enhancement of segregation of charged species to the boundary, where charge compensation is simpler.

Our calculations have considered grain boundaries in  $Fe_{1-x}O$  as a test case. From a variety of considerations, both theoretical (as from existing calculations for  $MgO:Fe$ , Stoneham and Sangster (1981)) and experimental data we suspected reaction (1) to have an especially low energy.  $Fe_{1-x}O$  is special in several respects. It is one of a group of oxides with the NaCl structure, all of which (MnO, FeO, CoO and NiO) are cation-deficient under normal conditions. Indeed,  $Fe_{1-x}O$  is stable against separation into  $\alpha$ -Fe and  $Fe_3O_4$  only above 840 °C, and has a homogeneity range from  $x = 0.05$  to 0.15.

There is a fundamental optical absorption edge near 2.4 eV (Bowen *et al* 1975) which is probably associated with a charge-transfer transition (Catlow and Muxworthy 1978). The charge-transfer reactions (1) that we shall consider will be thermal, rather than optical, and so may not precisely correspond to the 2.4 eV transition; nevertheless, this energy gives a useful reference value.

The new feature associated with grain boundaries is that cation sites are no longer equivalent. In the bulk perfect crystal, the Madelung potential is the same at each cation site. Near a grain boundary, variations in Madelung potential render certain sites significantly more attractive to electrons or to holes. It is these sites that lead to lower energies for electron transfer. As has been emphasised in previous work (Stoneham and Sangster 1981, Catlow and Muxworthy 1978), the lattice relaxation and polarisation energies are important components, and methods for calculating these near grain boundaries have only recently become available.

## 2. Methods for energies of reaction

### 2.1. Energy cycles

Systematic analysis for stability under reaction (1) is most easily examined using an energy cycle. This, like the Born–Haber cycle, breaks the reaction into a number of simpler steps for which energy contributions can be calculated. Stoneham and Sangster (1981) discussed the several contributions in detail; for present purposes, we shall concentrate on the dominant ones, namely the ionisation potentials and the polarisation energies. Thus, following Stoneham and Sangster, we look at the magnitude of  $\tilde{U}_{\alpha\beta}$  defined by

$$\tilde{U}_{\alpha\beta} = (I_{N+1}^{\alpha} - I_N^{\beta}) + (E_{N+1}^{\alpha} + E_{N-1}^{\beta} - E_N^{\alpha} - E_N^{\beta}) \quad (2)$$

for electron transfer from species  $\alpha$  to species  $\beta$ . Here  $I_N$  is the ionisation potential ( $M^{(N-1)+} \rightarrow M^{N+} + e_{\infty}$ ) and  $E_{N+M}$  is the energy needed to remove a host cation (for which  $N = 2$  in our case) and replace it by an ion of charge  $N + M$  (here either 3 or 1 in our case) with lattice polarisation and distortion. Expression (2) is sufficiently general to include impurities in several possible initial charge states. If, however, we consider only host cations initially in their usual charge state, we have

$$\tilde{U} = (I_3 - I_2) + E_3 + E_1 \equiv \tilde{U}_I + \tilde{U}_R$$

since  $E_2$  is zero. We have defined  $\tilde{U}_I$  solely in terms of ionisation potentials and  $\tilde{U}_R$  in terms of polarisation and distortion energies. For Fe,  $(I_3 - I_2)$  is 14.46 eV; for Ni it is 17.01 eV (Moore 1949).

### 2.2. Polarisation and distortion energies

Our work follows naturally the calculations of the structures and energies of several  $\langle 001 \rangle$  and  $\langle 011 \rangle$  tilt boundaries in NiO (Duffy and Tasker 1982a, b). These calculations used Tasker's (1979) MIDAS code, developed for the simulation of planar defects (such as surfaces or shear planes) in ionic crystals. It exploits a two-dimensional lattice summation technique (Parry 1975, 1976). The parameters for the interatomic potential, including both the Buckingham short-range terms and the core–shell interaction, were taken from Sangster and Stoneham (1981). The present work keeps the ionic radii

constant for the several charge states. The tilt boundary is modelled by rotating the crystal above and below the interface until the two relevant crystallographic directions are parallel to the [001] direction in some external coordinate system. For high-coincidence orientations there is two-dimensional periodicity in the boundary plane, and the Coulomb energy of the defect can be calculated using the lattice sums developed by Parry (1975, 1976). The relaxation procedure was initiated from several different displacements of the two grains in order to ensure that the final configuration was the true minimum.

For each representative type of tilt boundary, we calculated Madelung potentials for the (relaxed) ions close to the boundary. By inspection, one can identify the sites with the highest and lowest Madelung potentials. Charge transfers take place from the sites with the highest values to those with the lowest. We may make these transfers so that 3+ ions are at the sites with high Madelung energy and 1+ ions at the low-Madelung-potential sites. The grain boundary is then relaxed to equilibrium. The change in total energy gives us  $\bar{U}_R$  for the grain boundary. This term, being the sum of a Madelung contribution and a relaxation energy, is always negative. Only when  $|\bar{U}_R|$  exceeds  $|\bar{U}_I|$  is there an instability against charge disproportionation.

The explicit calculations, in which all ions near the grain boundary are relaxed to equilibrium both before and after charge transfer, allow us to check some much simpler calculations for the same energies  $\bar{U}_R$ . We have been able to verify:

(1) that the spread in Madelung potentials  $\Delta M$  at a given grain boundary is essentially the same in NiO and FeO, the slightly different lattice parameter and force constants having very little effect;

(2) that the change in  $\bar{U}_R$  from the value in the bulk,  $\bar{U}_{R0}$  is dominated by  $\Delta M$ , so that only one relaxed grain boundary geometry need be calculated.

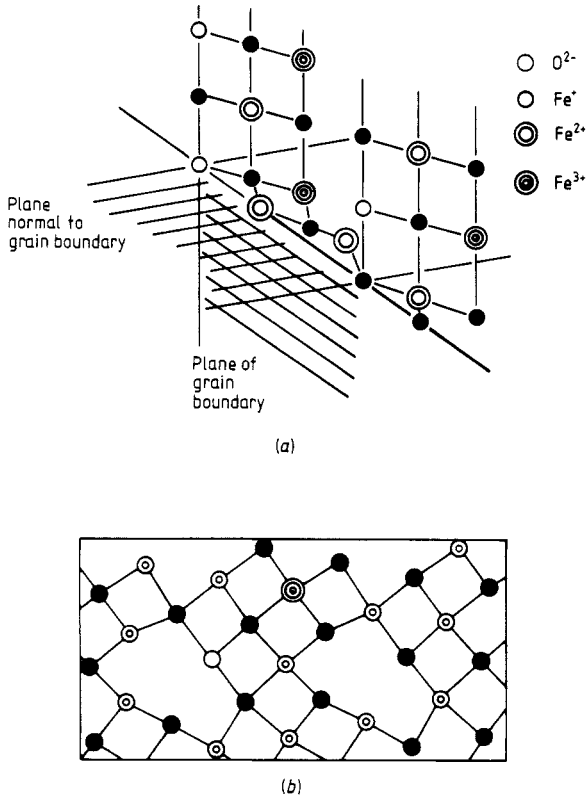
The first result is not too surprising, given the similarities among the cubic transition-metal oxides. The second point needs explicit verification, for there are three contributions to  $\bar{U}_R - \bar{U}_{R0}$ . The first is  $\Delta M$ ; the second arises because the 3+ and 1+ ions, separated by distance  $R$ , interact with energy of order  $e^2/\epsilon_0 R$ , which is small but non-zero. The third, which proves completely negligible, is the difference in relaxation energy around a 3+ (or 1+) ion depending on whether it is in the bulk crystal or at a grain boundary.

The second ((3+)-(1+) interaction) term can be obtained in two ways: one is to include the interaction both in the bulk case and in the grain boundary case; the other is to use estimates of  $\epsilon_0$  and  $R$ . We may see how these compare for the (320)/[001] boundary in NiO (figure 1). Here  $U_{R0}$  is -11.99 eV (separated 3+, 1+) or -12.11 eV (paired 3+ and 1+), corresponding to a 0.12 eV interaction term;  $e^2/\epsilon_0 R$  is about 0.2 eV. Another approach is to compare  $U_R - U_{R0}$  (both with paired 3+, 1+) for the fully relaxed grain boundary and bulk cases with the corresponding  $\Delta$ . The full relaxation calculation gives  $U_{R0}$  as -12.11 eV and  $U_R$  as -13.70 eV, i.e.  $U_R - U_{R0}$  is 1.59 eV. The value of  $\Delta M$  is 1.49 eV, differing only by 0.1 eV from  $U_R - U_{R0}$ .

Since our calculations already leave out small terms (e.g. Jahn-Teller energies) of order 0.1 eV, most of our results are based on estimates of  $\Delta M$  only.

### 2.3. Results for NiO and FeO

Since most of the interest in oxide grain boundaries, and hence most data, are for NiO (e.g. Atkinson and Taylor 1981), we looked initially at a wider variety of boundaries for this system, repeating promising cases for FeO. The results in table



**Figure 1.** The (320)/[001] boundary in FeO, shown after disproportionation: (a) perspective diagram; (b) section perpendicular to the grain boundary plane.

1 are for the (310)/[001], (210)/[001], (320)/[001] and (122)/[0 $\bar{1}$ 1] interfaces. The important factors are first the energies, i.e. the amount  $\Delta M$  by which the Madelung potentials are changed, and secondly the distances involved. If the charge exchange is over a short distance, then it will contribute more to optical absorption and conductivity. The situation is this for NiO:

(310)/[001],  $\Delta M \approx 0.74$  eV, sites share two oxygens, and are separated by  $\sqrt{2}$  nearest-neighbour distances;

(210)/[001],  $\Delta M \approx 0.33$  eV, sites share two oxygens, and are separated by  $\sqrt{2}$  nearest-neighbour distances;

(320)/[001],  $\Delta M \approx 1.49$  eV, sites separated by about twice the nearest-neighbour spacing, sharing a common oxygen;

(122)/[0 $\bar{1}$ 1],  $\Delta M \approx 1.23$  eV, sites separated by about  $\sqrt{2}$  times the nearest-neighbour distance, sharing two oxygens.

The spread in Madelung potentials suggests that the (320)/[001] boundary is the most favourable for charge disproportionation. We have made explicit calculations for this boundary in FeO and NiO, confirming 'negative  $U$ ' behaviour in FeO only:

$$\text{FeO:} \quad \bar{U}_I = 14.46 \text{ eV} \quad \bar{U}_R = -15.17 \text{ eV} \quad \bar{U} = -0.71 \text{ eV}$$

$$\text{NiO:} \quad \bar{U}_I = 17.01 \text{ eV} \quad \bar{U}_R = -13.70 \text{ eV} \quad \bar{U} = +3.31 \text{ eV.}$$

**Table 1.** Maximum ( $2M_{\max}$ ) and minimum ( $2M_{\min}$ ) Madelung energies (in eV) for cations close to tilt boundaries in NiO<sup>†</sup>

Boundary	Misorientation angle (deg)	$\Sigma$	$2M_{\max}$	$2M_{\min}$	$2\Delta M$
(310)/[001]	36.9	5	48.85	47.38	1.47
(210)/[001]	53.1	5	48.52	47.87	0.65
(320)/[001]	67.4	13	49.20	46.23	2.97
(122)/[011]	38.9	9	49.49	47.02	2.47

<sup>†</sup> Note that, since the ionic charge is 2, an electron making a transfer from a site with maximum Madelung energy to one with the minimum value gains energy  $\Delta M$ , not  $2\Delta M$ ; this comes simply from the convention defining Madelung energies. Thus  $2\Delta M$  refers to the ionic Madelung energy in eV, and  $\Delta M$  refers to the Madelung potential in volts.

### 3. Discussion

Much of the experimental data on Fe<sub>1-x</sub>O relevant here is complex and often on poorly characterised samples. Nevertheless, it is useful to look at the implications of our results. First, in Fe<sub>1-x</sub>O, we predict that Fe<sup>3+</sup> and Fe<sup>2+</sup> will form spontaneously at certain grain boundaries. This should show in Mössbauer and perhaps in magnetic resonance experiments. Secondly, even when the grain boundary cations are stable in their 2+ charge state, there will be excitations of low energy giving 3+ and 1+ states. These will include the disproportionation reaction, as well as straightforward ionisation:



since the altered Madelung potential contributes to the ease of ionisation. Even if instabilities are absent (as in Ni<sub>1-x</sub>O for instance), we anticipate that grain boundaries will provide an excess electrical conductivity, just as they offer fast diffusion paths. Again, as in diffusion, we expect grain boundaries to have most effect at low temperatures, when the lower carrier formation energies outweigh the smaller fraction of ions that are available for ionisation. Thirdly, the variations in Madelung potentials will affect impurity segregation: certain sites will strongly favour impurities with positive excess charge, others with negative excess charge. Fourthly, the modulation of the Madelung potential may encourage new phases to develop near grain boundaries, associated either with impurities or merely with structural disorder in these non-stoichiometric systems. In particular, the (4:1) clusters, which are the basic defect units of M<sub>1-x</sub>O oxides (see Catlow and Stoneham (1981) for discussion and references) may be encouraged to order in different ways.

Experimentally, the position is complicated. One important result is that grain size makes *no* significant difference to higher-temperature (1000–1300 °C) electrical conductivity or Seebeck coefficient (Hillegas and Wagner 1967). These temperatures are sufficiently high that grain boundaries are not major contributors to diffusion either, so it is perhaps useful to turn to low-temperature data. Even single-crystal data are complex (Bowen *et al* 1975) and it is harder still to identify clearly the mechanisms reported by other workers (Balberg 1974, Eremenko *et al* 1976) except to say that there is limited evidence of enhanced conductivity. Given the difficulties of detailed interpretation (see e.g. Kofstad (1972) for a survey) it is hard to say more than that a grain boundary contribution to the conductivity may be present at lower temperatures.

One final general point is worth emphasising. Most interfaces in polar crystals can encourage the formation of unusual charge states. There are two factors. One is the inhomogeneity of Madelung potentials, as discussed here. The other is the image potential. Suppose there is a boundary between media of dielectric constants  $\epsilon_L$  and  $\epsilon_S$ , with  $\epsilon_L > \epsilon_S$ . Then a point charge  $Z|e|$  in the medium of smaller dielectric constant  $\epsilon_S$  and at distance  $d$  from the interface will be stabilised by an energy  $Z^2e^2/4\epsilon_{\text{eff}}d$  with  $\epsilon_{\text{eff}} \equiv \epsilon_S(\epsilon_S + \epsilon_L)/(\epsilon_L - \epsilon_S)$ . We stress that the image term requires only a change in  $\epsilon$ , irrespective of whether the other medium is metal, non-metal or vacuum; we also stress that the image term is quite distinct from any straightforward difference between surface and bulk Madelung potentials. This image term contributes an energy  $Z^2e^2/2\epsilon_{\text{eff}}d$  encouraging disproportionation, for example, since both positive and negative charges benefit. For a metal-insulator interface  $\epsilon_{\text{eff}}$  is just  $\epsilon_S$ , since the larger metal dielectric constant,  $\epsilon_L$ , is essentially infinite. This allows us to make direct contact with Harrison's (1976) discussion proposing that negative- $U$  instabilities were involved in Schottky barrier behaviour. Whilst FeO and NiO are of no real interest as Schottky barriers, the same effects on the charge states may influence oxidation rates through their control of processes at the interface between the metal and the oxide.

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