Atomic Structure of Symmetric Tilt Grain Boundaries in NiO

K. L. Merkle
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439
and
David J. Smith
Center for Solid State Science and Department of Physics, Arizona State University, Tempe, Arizona 85287
(Received 22 October 1987)

High-resolution electron microscopy shows the coexistence of several distinct core structures for coincident-site lattice boundaries in NiO bicrystals near $\Sigma=5$, (310), and $\Sigma=13$, (510), where Σ is the reciprocal density of coincident lattice sites. Lattice expansion perpendicular to the $\Sigma=5$ grain boundaries is considerably smaller than calculated theoretically. Structural units in boundaries near $\Sigma=13$, (510) exhibit translations normal to the grain-boundary plane, resulting in a rumpling of the interface on an atomic scale. Our observations suggest the presence of a high concentration of Schottky pairs in the grain boundaries.

PACS numbers: 61.16.Di, 61.70.Ng

Atomic-level information on the core structure of grain boundaries (GB's) has largely been derived from computer simulations.[1,2] With the advent of the latest generation of high-resolution electron microscopes (HREM's) it has become possible, for a wide range of materials, to deduce atomic-structure models directly from experimental observation. In this Letter we report a preliminary analysis of the core structure of $\Sigma=5$, (310) and $\Sigma=13$, (510) ⟨001⟩-tilt GB's in NiO. Several of our observations are of particular significance: (1) Several different core structures exist for each GB; (2) asymmetric structural units are quite common, even in symmetric GB's; (3) the $\Sigma=13$ boundary deviates, on an atomic scale, from a planar configuration in analogy to surface roughening or surface reconstruction. It is likely that some of these structural features are not only typical of high-purity ceramic oxides, but they could also apply to large-angle GB's in general.

The coincident-site lattice (CSL) GB's, which are characterized[3] by the reciprocal density of coincident lattice sites Σ, have received considerable attention in studies of GB's. In recent years GB theory has often used the molecular-statics approach in order to calculate the energies and structures of GB's in metals and ionic solids.[1,2] Symmetric CSL boundaries have been investigated almost exclusively, although it has become apparent that asymmetrical GB's, notably those for which a low-index plane borders the GB, play an important, and perhaps dominating, role in the large-angle regime.[4,5] Symmetric, low-Σ, CSL boundaries have an advantage in that they contain the smallest repeat units. Such GB's are thus most easily amenable to detailed studies of the core structure by means of computer simulation as well as by HREM.

Bicrystal specimens of NiO were prepared by the Verneuil technique, as described previously.[6] Care was taken to ensure chemical purity and stoichiometry. The bicrystals were quenched to room temperature from 1373 K and standard ion-milling techniques were used to produce suitably thin sections. The specimens were observed in a JEOL model 4000EX HREM at 400 kV with axial illumination with use of a concentric objective aperture corresponding to $\simeq 1$ Å^{-1}. Micrographs were typically taken at several defocus values and at magnifications of 600000× and 800000×.

In Fig. 1, one section of a (310) GB, recorded near the optimum defocus where atomic columns appear black, clearly shows a transition between different core structures, labeled A and B, as the boundary plane translates from one facet to the next. Figure 2 shows the structures A and B together with averaged structural units which were generated by superimposing four structural units present in the experimental micrograph, by use of a digi-

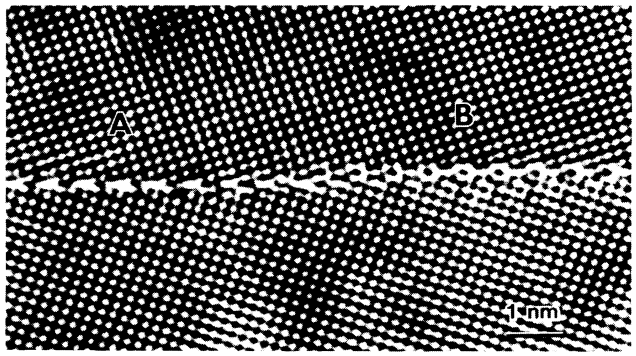

FIG. 1. Atomic resolution electron micrograph of a ⟨001⟩ symmetric tilt grain boundary in NiO close to $\Sigma=5$, (310), taken near optimum defocus (dark atomic columns). As the boundary translates from the left facet to the right one, the core structure changes from structure A to structure B.

© 1987 The American Physical Society

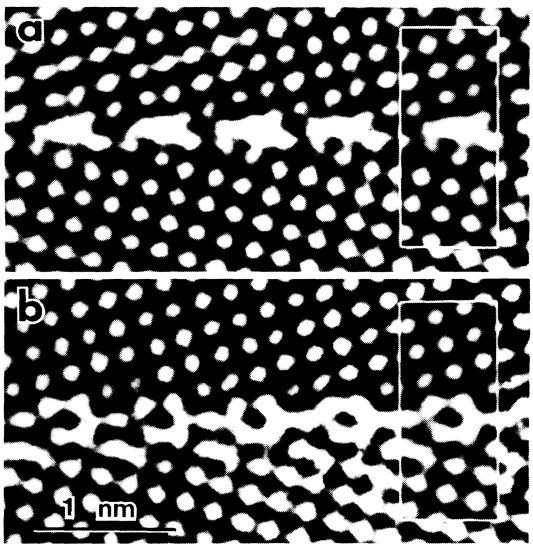

FIG. 2. Enlargements showing (a) structure A and (b) structure B are recorded, together with averaged structures shown as insets.

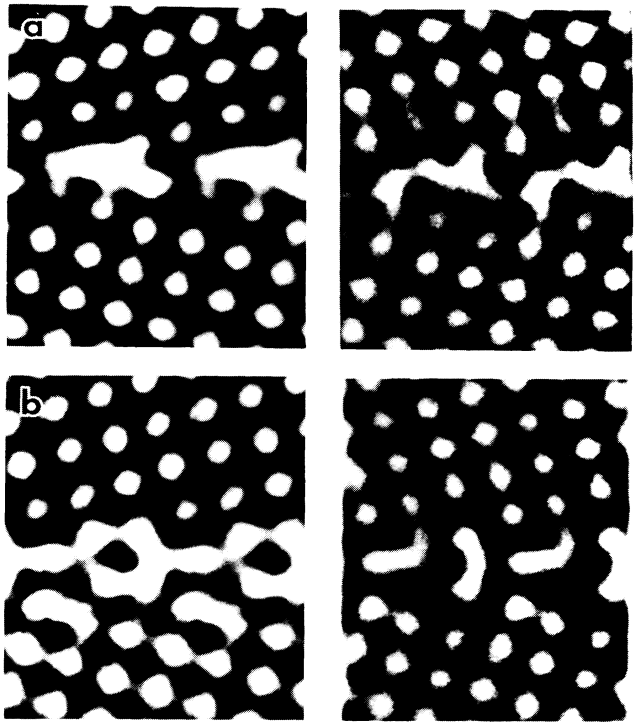

FIG. 3. Averaged experimental images of $\Sigma=5$ GB compared to image simulations (thickness 42 Å, defocus -400 Å). (a) structure A; (b) structure B.

tal frame store. Atomic models which are consistent with these observed images can be verified by comparisons with image simulations. However, accurate simulations require a knowledge of the thickness and the objective-lens defocus. By our viewing the GB at a large tilt under conventional imaging conditions, the thickness was determined to be near 40 Å. We were also able to confirm that the defocus value was close to optimum by performing a two-dimensional Fourier transform from a large region of the image near that shown in Fig. 1.

Figure 3 displays two unit cells of each of the averaged images of structures A and B and compares them with computer-generated images obtained through multislice image calculations.[7] The positions of the atomic columns used in the simulation were obtained from the coordinates of the centers of the dark regions present in the image recorded near optimum defocus. This procedure gives reasonably good agreement between experimental and calculated images. However, minor differences, particularly in the appearance of the open spaces at the core, can be noted and will be discussed below.

The arrangement of the atomic columns observed by HREM is distinctly different from atomic structures[8,9] of the (310) boundary in cubic oxides proposed previously (see Fig. 4). The most striking feature of the structure obtained from lattice-statics calculations by Duffy and Tasker[9] is the presence of large open spaces at the core of the boundary. A considerable reduction in the local atomic density has also been implied by observations of the defocus contrast by conventional transmission electron microscopy.[10] Although some degree of openness is apparent at the core of the GB's observed by HREM, the volume expansion is considerably less than in the lattice-statics result. The lattice expansion perpendicular to the GB is 0.4 and 0.3 Å for structures A and B, respectively. The structure of Duffy and Tasker, which corresponds to an expansion of 1.1 Å, has, roughly speaking, one (620) plane missing relative to the structures derived from experiment.

The arrangement of atoms in structure B is closer to

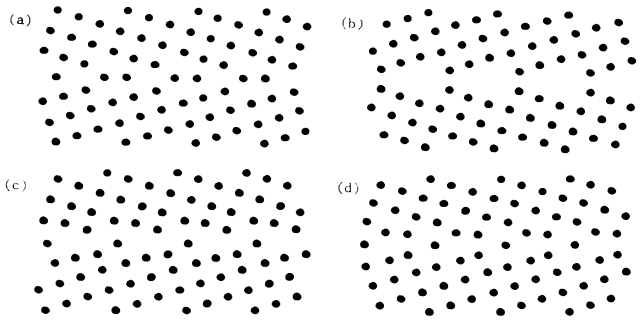

FIG. 4. Grain-boundary models for $\Sigma=5$, (310) in NiO. (a) Kingery (Ref. 8), (b) Duffy and Tasker (Ref. 9), (c) structure A, and (d) structure B.

being symmetric, although distinct deviations from mirror symmetry can be noted for atoms close to the core. The positions of the atoms at the periphery of the core region are near those in the structure calculated by Duffy and Tasker. Structure A, which is strikingly asymmetric, can be thought of as resulting from the symmetric configuration by a translation of 2.9 Å parallel to the boundary plane.

The small lattice expansion for both structures, which is only a factor of 1.5 to 2 greater than the densest packing in a hard-sphere model,[11] is quite surprising in view of the strong Coulomb interactions in ionic solids. The latter prohibit the close proximity of like ions and are thought to be responsible for a rather open GB structure in ionic solids.[9] In comparison with metals, large-angle GB's in NiO show stronger Fresnel contrast effects as a function of defocus in kinematical bright-field images, which is indicative of a correspondingly greater reduction in atomic density at the GB.[10] As an alternative to the presence of large open channels, a substantial reduction in atomic density at the GB could be accomplished by the presence of Schottky pairs, i.e., pairs of anion and cation vacancies, in the atomic columns bordering the core. As illustrated in the next paragraph, individual columns which appear not fully dense are occasionally observed. Moreover, on close examination of Fig. 3, it can be seen that the cores appear more open in the experimental images relative to the simulations, which assume fully dense columns at the GB. Theoretical investigations on twist boundaries in NiO have found a considerable decrease in GB energy when Schottky pairs are introduced into the GB plane.[12,13] The present observations indicate that vacancy-type defects may also play an important role in tilt GB's. A quantitative evaluation of the effective atomic density at the boundary is beyond the scope of the present Letter, but could be based on detailed HREM-image simulations or an analysis of the bright-field defocus contrast.

A section of a $\Sigma=13$, (510) boundary is shown enlarged in Fig. 5. Three different geometries of the core structure can be recognized. In addition, we find displacements of the core centers perpendicular to the average GB plane. One of the core structures is shown enlarged in Fig. 6. The image contrast from two of the columns bordering the core is noticeably weaker than the contrast of a typical column. Simulations of the core images, based on a reduced occupancy of individual columns, indicate that such changes in contrast could result from a vacancy content of $\simeq 25\%$.

Another important feature of this core concerns the possible ionic charge distributions at individual core structures. The latter can be viewed as $a\langle 100\rangle$-type dislocations, where a is the lattice parameter. In the bulk of each crystal, anions and cations alternate between nearest-neighbor atoms. Since the two crystals are smoothly connected in between the cores, a given pattern of ionic-charge distribution is carried through both crystals on any given (002) plane. When making possible assignments of anions and cations based on the observed projected structure in Fig. 6, one is always left, near the core, with a triplet of like charges next to each other, for example centered at C or D in Fig. 6. Since strong Coulomb repulsions render such a configuration extremely unfavorable energetically,[9] we conclude that at least one of the columns must be displaced along the

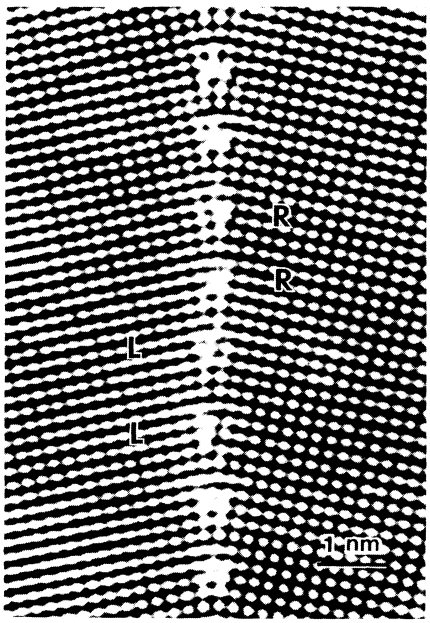

FIG. 5. Symmetric ⟨001⟩ tilt grain boundary in NiO near $\Sigma=13$, (510). Note the differences and asymmetries in the core structures. Cores R are displaced to the right, and cores L to the left, of the average GB plane.

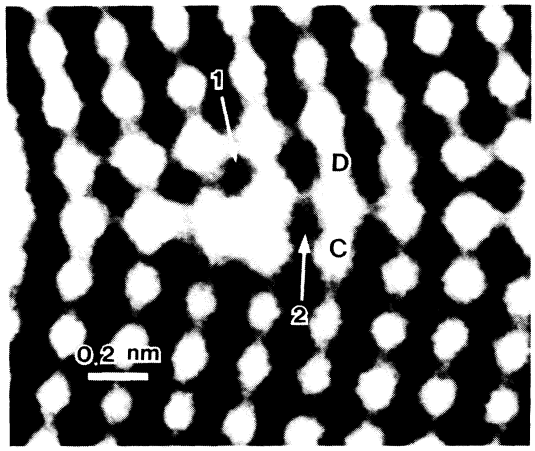

FIG. 6. Enlargement showing one of the basic structural units visible in Fig. 5. Columns 1 and 2 show reduced contrast. A triplet of like ionic charges could be centered at C or D.

direction of the misorientation axis.

The origin of the differences in structure relative to theoretical models of GB's is not known. Since the present GB structures were essentially frozen in at temperatures near 1400 K, it is possible that 0-K calculations, which neglect entropy effects, may be inappropriate. Lattice-statics calculations on metals[14] and oxides[9,13] generally give several metastable structures of large-angle GB's that are close in energy and thus predict the multiplicity of structures that has been reported here.

We are pleased to acknowledge the assistance of J. F. Reddy and C. L. Wiley as well as helpful discussions with D. Wolf. This work has been supported by the National Science Foundation through Grant No. DMR-830871, and by the U.S. Department of Energy, Basic Energy Sciences, under Contract No. W-31-109-Eng-38.

[1]Proceedings of the Symposium on Computer Simulation in the Study of Solid-Solid Interfaces, Philadelphia, Pennsylvania, 1983, edited by P. D. Bristowe and R. J. Harrison, Surf. Sci. **144**, No. 1 (1984).

[2]See papers in Proceedings of the International Conference on the Structure and Properties of Internal Interfaces, Irsee, Germany, 1984, edited by M. Rühle, R. W. Balluffi, H. Fischmeister, and S. L. Sass, J. Phys. (Paris), Colloq. **46**, C4 (1985).

[3]W. Bollmann, *Crystal Defects and Crystalline Interfaces* (Springer-Verlag, Berlin, 1970).

[4]D. Wolf, J. Phys (Paris), Colloq. **46**, C4-197 (1985).

[5]K. L. Merkle and D. J. Smith, Ultramicroscopy **22**, 57 (1987).

[6]K. L. Merkle, J. R. Reddy, and C. L. Wiley, Mater. Res. Soc. Symp. Proc. **41**, 213 (1985).

[7]The image simulations were performed with use of the Melbourne University suite of programs, adapted for large unit cells. Simulation parameters appropriate for the JEOL model 4000 EX at Arizona State University were used.

[8]W. D. Kingery, J. Am. Ceram. Soc. **57**, 1 (1974).

[9]D. M. Duffy and P. W. Tasker, Philos. Mag. A **47**, 817 (1983), and **48**, 155 (1983).

[10]K. L. Merkle, J. F. Reddy, and C. L. Wiley, J. Phys. (Paris), Colloq. **46**, C4-95 (1985).

[11]H. J. Frost, M. F. Ashby, and F. Spaepen, Scr. Metall. **14**, 1051 (1980).

[12]P. W. Tasker and D. M. Duffy, Philos. Mag. A **47**, L45 (1983).

[13]D. Wolf, Mater. Res. Soc. Symp. Proc. **24**, 47 (1984).

[14]Gui Jin Wang, A. P. Sutton, and V. Vitek, Acta Metall. **32**, 1093 (1984).

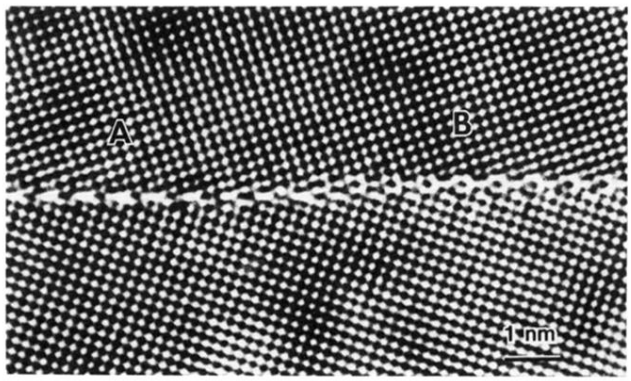

FIG. 1. Atomic resolution electron micrograph of a ⟨001⟩ symmetric tilt grain boundary in NiO close to $\Sigma=5$, (310), taken near optimum defocus (dark atomic columns). As the boundary translates from the left facet to the right one, the core structure changes from structure A to structure B.

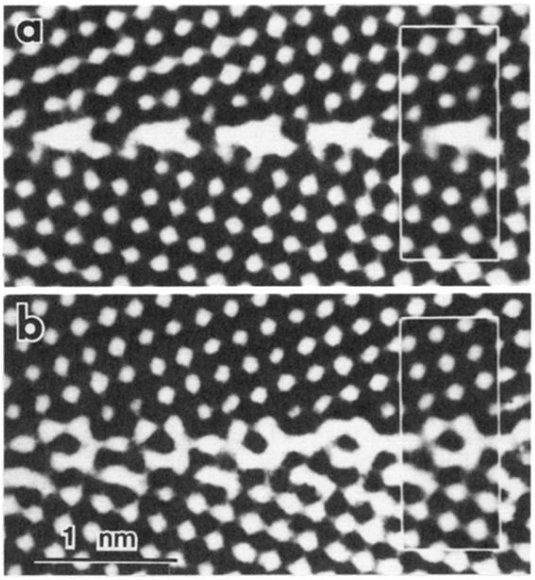

FIG. 2. Enlargements showing (a) structure A and (b) structure B are recorded, together with averaged structures shown as insets.

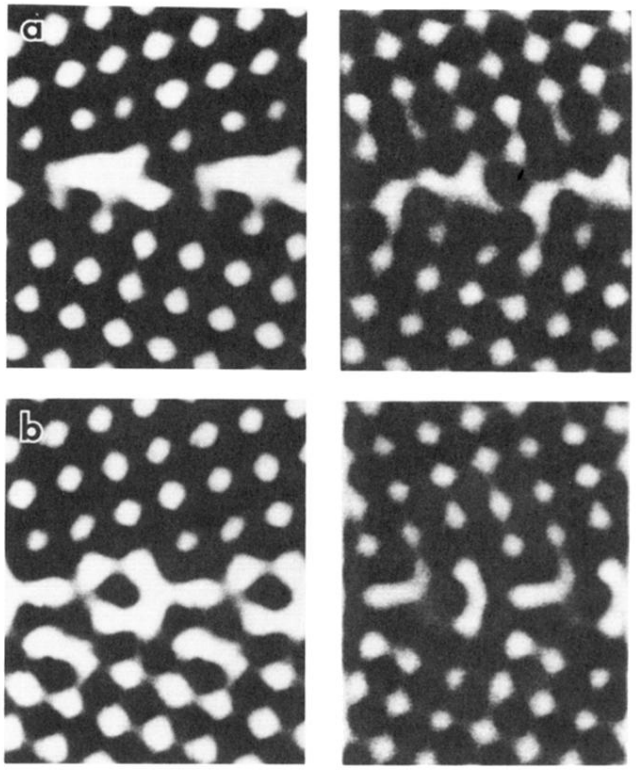

FIG. 3. Averaged experimental images of $\Sigma=5$ GB compared to image simulations (thickness 42 Å, defocus -400 Å). (a) structure A; (b) structure B.

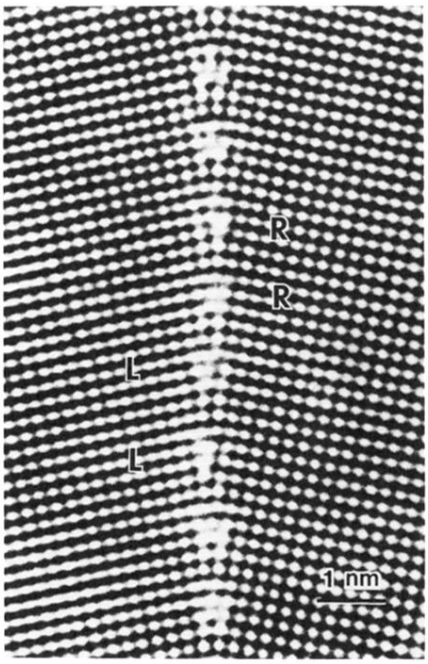

FIG. 5. Symmetric ⟨001⟩ tilt grain boundary in NiO near $\Sigma=13$, (510). Note the differences and asymmetries in the core structures. Cores R are displaced to the right, and cores L to the left, of the average GB plane.

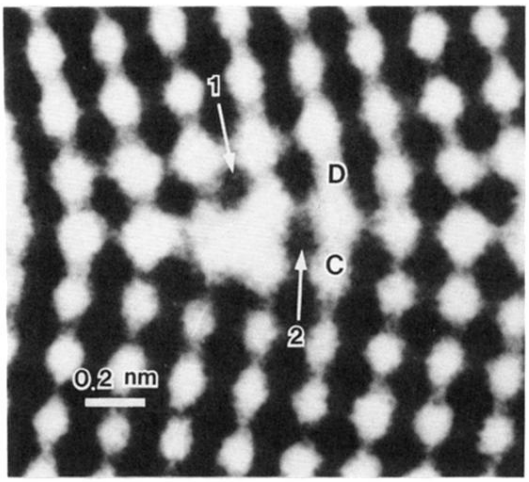

FIG. 6. Enlargement showing one of the basic structural units visible in Fig. 5. Columns 1 and 2 show reduced contrast. A triplet of like ionic charges could be centered at C or D.