

### Rippled Relaxation in the (110) Surface of the Ordered Metallic Alloy NiAl

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Results from a LEED analysis of NiAl(110) demonstrate that it possesses a large rippled relaxation away from its hypothetical truncated bulk surface, with the Al sites of the top composite Ni-Al layer being displaced approximately 0.22 Å above the Ni sites. The evidence for this rippling is strong, since the agreement achieved between calculated and experimental *I-V* profiles is of the same quality obtained in better LEED analyses of monatomic surfaces.

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In this Letter, a brief description is presented of a low-energy electron-diffraction (LEED) analysis of the (110) surface of the ordered metallic alloy NiAl. Since NiAl has the CsCl structure, its hypothetical truncated bulk surface would consist of composite layers, parallel to the surface, with each layer containing half Ni and half Al sites which are exactly coplanar (see Fig. 1). However, an intriguing, and perhaps surprising, result from our LEED analysis is that the actual NiAl(110) surface possesses a relatively large rippled relaxation where the Al sites of the top composite layer are displaced above the Ni sites by approximately 0.22 Å (see Fig. 2). Although some results from previous investigations of insulating *AB*-type compounds have suggested different relaxations for *A* and *B* surface sites

[e.g., LiF(100)],<sup>1</sup> to our knowledge, the results for NiAl(110) provide the first demonstration that different, and relatively large, relaxations exist in the surface of an ordered metallic alloy. Also, the present results must be considered as being much more than a speculative postulation, since the evidence for the rippled relaxation is strong.

Our motivations for investigating NiAl(110) were twofold. First, the necessary single crystal was readily available from Ford *et al.*,<sup>2</sup> who have performed an angle-resolved photoemission study of NiAl. Also, auxiliary studies conducted by them showed that it was possible to obtain a reasonably sharp LEED diffraction pattern from the NiAl(110) surface, which was a necessary, but not sufficient, condition to believe that a LEED structural analysis might be successful. Our second motivation was that conducting an analysis of the surface of an ordered metallic alloy would be a logical extension of several recent LEED analyses,<sup>3-9</sup> concurrent with which there also have been high-energy ion-scattering (HEIS) investigations<sup>10,11</sup> of surfaces of some monatomic metals. The thrust of these investigations was to determine the amount of layer relaxation present in unreconstructed metallic surfaces. Layer relaxation is a rigid movement of one, or more, of a surface's atomic layers away from their positions in the hypothetical truncated bulk surface (without change of atomic positions in the layers). Depending upon the symmetry of the surface, the layers' movements can have components both perpen-

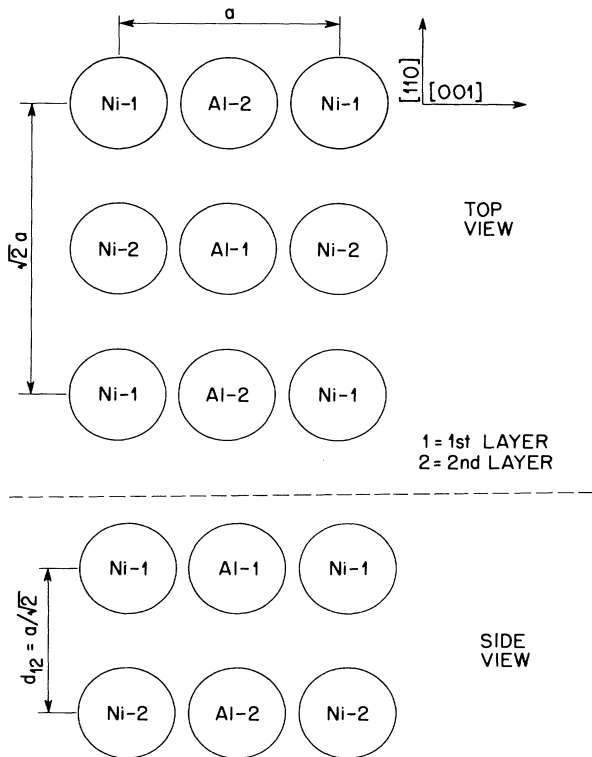


FIG. 1. Truncated bulk surface for NiAl(110).

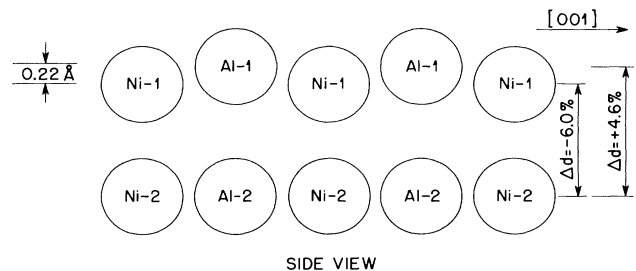


FIG. 2. Rippled surface for NiAl(110) as indicated by the results of the present LEED analysis.

dicular and parallel to the surface. Also, measurable relaxation can extend down to the third or fourth layers of some surfaces. Thus, the determination of the relaxations of NiAl(110) would add a new dimension to the experimental information available for metallic surfaces, and could then motivate extensions of existing theories for monatomic metals to be made for alloys.

Although most of the theoretical treatments would apply, strictly speaking, to *s-p* bonded metals, a consistent theoretical explanation is emerging for the layer relaxations of monatomic metallic surfaces. For example, most investigated surfaces have a smaller spacing between the first and second layers,  $d_{12}$ , than between bulk layers. Such a contraction in  $d_{12}$  is consistent with a simple theory of Finnis and Heine,<sup>12</sup> which explained the inward relaxation of the first layer as the response to electrostatic forces produced by a smoothing of the surface's electronic density. This idea has been extended,<sup>13</sup> with detailed model-type calculations, to show that the forces would also produce deeper layer relaxation. This work also predicted a damped oscillatory relaxation in the spacings between layers of low-index surfaces, which is consistent with recent LEED analyses.<sup>3-9</sup> The theory has been now extended<sup>14</sup> to have more of a first-principles character, and its predictions for Al(110) are in relatively good agreement with two very recent LEED analyses.<sup>5,7</sup> Also, some model-type calculations performed<sup>15</sup> for high-index surfaces indicate that they should have layer relaxations with both perpendicular and parallel components, as have been observed for the (210), (310), and (211) Fe surfaces<sup>8</sup> and W(211).<sup>16</sup> To date, no extensions of the theoretical concepts have been made to ordered alloy surfaces.

The procedures used to prepare the NiAl(110) surface for our LEED analysis are too detailed to be described here; however, a very good surface was obtained with large and well-ordered domains. A semi-quantitative Auger analysis indicated that it contained approximately half Ni and half Al sites. Also, the surface produced a sharp (1×1) LEED diffraction pattern, whose sharpness was better than we observed for the Al(110) surface.<sup>5</sup> With the incident electron beam normal to the surface, intensity versus voltage (*I-V*) profiles were collected for energies up to 300 eV. A total of fourteen *I-V* profiles were collected, which were all the profiles in the symmetrically equivalent {01}, {10}, {11}, {12}, and {20} sets. The two diffraction beams of the {01} set were in a plane containing the longer side of the rectangular unit cell of NiAl(110). The individual members of each {*ij*} set were compared with each other and found to be in good, but not perfect, agreement. Equivalent beam averaging (EBA)<sup>17</sup> was then applied to the data base to obtain five EBA experimental profiles to use in the

subsequent analysis.

The five EBA profiles were compared with the results of numerous sets of dynamical LEED calculations. The necessary computer codes were constructed in a manner first to calculate scattering matrices for composite Ni and Al layers. These matrices are defined by Eq. (4.49) of Pendry,<sup>18</sup> and the codes were constructed such that the Ni and Al sites of a layer did not necessarily have to be coplanar. The multiple scattering between composite layers was treated by re-normalized forward scattering perturbation.<sup>18</sup> The calculations employed eight scattering phase shifts, obtained from either the Wakoh<sup>19</sup> potential for Ni or the Snow<sup>20</sup> potential for Al, and Debye temperatures of 335 and 550 K, respectively, for the Ni and Al sites. Up to 81 beams were used, and beam attenuation was mimicked with a constant 4.5 eV for the imaginary component of the optical potential.

The experimental *I-V* profiles were compared first with calculated profiles for the truncated bulk structure of NiAl(110). This comparison resulted in a value of 0.131 for the total, five-profile, Zanazzi-Jona<sup>21</sup>  $R_{ZJ}$  factor. A series of calculations was then performed where the Ni and Al sites were kept coplanar in each composite layer but relative changes in  $d_{12}$ , the spacing between the first and second composite Ni-Al layers, were made in the range -15% to +10%. The overall minimum  $R_{ZJ}$  value for this calculational series was 0.129, and occurred for  $\Delta d_{12} = -2.2\%$ . Thus variation of  $d_{12}$ , with Ni and Al sites kept coplanar, produced only a very slight reduction in  $R_{ZJ}$ . Also, no consistency was found in single-profile  $R$  factors as  $\Delta d_{12}$  was changed from 0% to -2.2%, since three of the five increased in value.

Since an  $R_{ZJ}$  value of about 0.13 might be considered as a respectable value for the final result of a LEED analysis,<sup>21</sup> it could incorrectly be concluded from the above results that the structure of NiAl(110) closely resembles the truncated bulk. However, no *a priori* reason exists to believe that the Ni and Al sites should be coplanar in the outermost composite layers. [The existence of the (1×1) spot diffraction pattern does not require the sites to be coplanar.] So a series of LEED calculations was performed where the positions of the Ni and Al sites in the first composite layer were varied, perpendicularly to the surface, but were not constrained to be coplanar. However, their individual lateral positions were maintained at those of the truncated bulk. A total of 81 sets of LEED calculations were performed where  $\Delta d_{12}(\text{Ni})$ , the change in perpendicular position of Ni sites relative to the spacing between bulk composite layers (=2.04 Å), was varied from -14% to +2% in increments of 2%, and  $\Delta d_{12}(\text{Al})$  was varied from -2% to +14%. Total  $R_{ZJ}$  values were then obtained from all 81 sets by comparison of calculated and experimental *I-V* profiles. The

energy range used in comparison of the (ten) profiles was 55 to 300 eV, and the total energy range for all five profiles was 1118 eV.

The above  $R_{Zj}$  have been used to construct Fig. 3, whose overall minimum of 0.053 is for  $\Delta d_{12}(\text{Ni}) = -6.0\%$  and  $\Delta d_{12}(\text{Al}) = +4.6\%$ . These  $\Delta d_{12}$ 's correspond to a rippled first-composite layer, where the Al sites are above the Ni sites by 0.22 Å (see Fig. 2). The evidence for such a large ripple is strong, since the  $R_{Zj}$  has been reduced by a factor of 2.4 from that for the best model where the Ni and Al sites were constrained to be coplanar. Also, all five individual profiles had their single-profile  $R$  factors reduced by, at least, a factor of about 2. Such consistency, among the beam analyses, must be considered as further evidence that a large rippled relaxation of the Ni and Al sites is a valid characterization of NiAl(110) and not just an artifact of the LEED analysis. A large ripple in the first composite layer might then indicate that measurable relaxation also exists in deeper composite layers. Preliminary investigations have been conducted and, even though the analysis is sensitive (i.e., assumed relaxations produce significant  $R_{Zj}$  changes), any relaxations present in deeper layers appear to be small. We expect to investigate this point in greater detail in a future analysis, which will employ a more extensive data base.

A set of  $I$ - $V$  profiles was calculated specifically for  $\Delta d_{12}(\text{Ni}) = -6.0\%$  and  $\Delta d_{12}(\text{Al}) = +4.6\%$ . Single-profile  $R$  factors for these were 0.031, 0.048, 0.064, 0.061, and 0.063 for, respectively, the (01), (10), (11), (12), and (20) profiles. These values would be

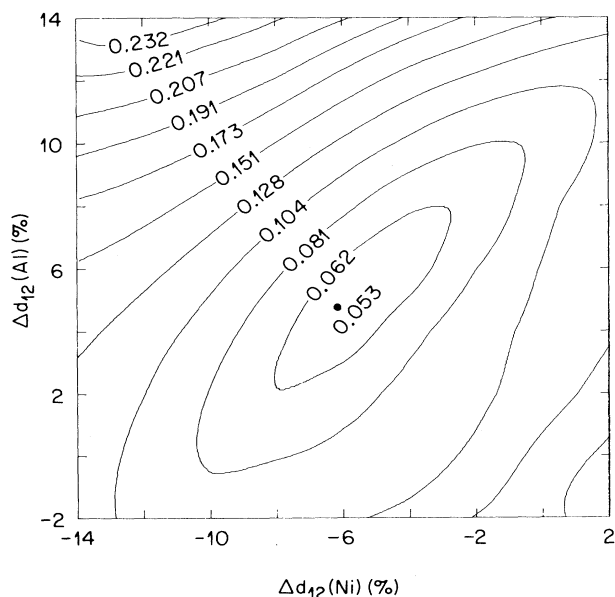


FIG. 3. Total  $R_{Zj}$  as a function of the perpendicular relaxations of the Ni and Al sites of the first composite layer.

considered<sup>21</sup> as quite small even for the analysis of the surface of a monatomic metal, which should serve to add some credibility to the present results. This is surprising, since features could exist in surfaces of ordered alloys (e.g., surface segregation, disordering of atomic components, etc.) which could degrade the agreement achievable between calculated and experimental  $I$ - $V$  profiles beyond that attainable for surfaces of monatomic metals. Our present opinion is that the small  $R_{Zj}$  is an indication that the NiAl(110) sample possessed a high degree of perfection.

It is anticipated that our demonstration of a large atomic rippling in NiAl(110) will motivate further research, both experimental and theoretical, on this and other surfaces. An investigation of NiAl(110) by some different experimental, structural technique, such as HEIS, would be of particular importance since LEED and HEIS are quite independent probes of surface structure. It is also desirable that the present theories<sup>13-15</sup> of surface relaxation be extended to ordered alloys, with such an extension hopefully furnishing plausibility arguments for the large atomic rippling found in NiAl(110). In this regard, the idea of Finis and Heine,<sup>12</sup> of smoothing a surface's electronic density, is easily extended to provide a qualitative plausibility argument for rippling in alloy surfaces whose atomic species have different core charges. Finally, since the first-appearing future theories probably will be quantitatively applicable to only surfaces of  $s$ - $p$  bonded alloys, obtaining structural information for such surfaces is of prime importance.

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