Atomic structure of a Gd(0001) surface

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A low-energy electron-diffraction intensity analysis of a clean Gd(0001) surface finds that this surface is relaxed, with the first interlayer spacing contracted by $3.5\pm1.0\%$ and the second interlayer spacing expanded by $2.0\pm1.0\%$ with respect to the bulk spacing (2.89 Å). This result is in partial agreement with one and in strong disagreement with another theoretical result of first-principles calculations by other authors, but fits well in the norm of what is known about basal-plane surfaces of most hexagonal close-packed metals.

I. INTRODUCTION

The growth of high-purity single crystals of the rare earths has long been a problem fraught with enormous experimental difficulties (see, e.g., Beaudry and Gschneidner[1]). The preparation of atomically clean surfaces of these elements is an even more difficult problem, not only because these materials are extremely reactive, but especially because impurities present in the bulk at levels of only a few parts per million have a strong tendency to segregate on the surface, thereby producing substantial surface coverages.

The relatively limited experience acquired so far[2,3] shows that the major contaminants found on the surfaces of high-purity rare-earth crystals are carbon, oxygen, and chlorine, all of which can be either eliminated (oxygen) or substantially reduced by appropriate noble-gas sputtering treatments. However, the necessary subsequent annealing treatments at intermediate temperatures, ranging, in the case of Tb, between 500 and 900 °C, usually causes the segregation on the surface of substantial amounts of iron, which is an impurity present in the bulk of high-purity single crystals of most rare earths at levels of 5–20 ppm. This surface segregation of iron can be very harmful to surface studies: for example, on an otherwise clean (0001) surface of Tb, the presence of a substantial fraction of a monolayer of iron has been shown to alter both the electron band structure and the atomic structure in significant ways.[4] Consequently, any experimental study of the physical properties of rare-earth surfaces must first be directed, more than for other metals, to finding an appropriate procedure for eliminating, or at least minimizing, the concentrations of impurities, and especially of iron, on the surface under scrutiny.

Several studies of the (0001) and the $(11\bar{2}0)$ surfaces of Y, Pr, Gd, Ho, and Er have been reported in the literature by the Liverpool group,[5,6] but they have not involved quantitative determinations of the surface atomic structure. Only three such determinations of rare-earth surfaces have been published, all three by means of quantitative analysis of low-energy electron-diffraction (LEED) intensities, namely, those of Sc(0001) (Ref. 7), Tb(0001) (Ref. 3), and Tb$(11\bar{2}0)$ (Ref. 8). All three surfaces were found to be relaxed, and the (0001) surfaces, in particular, were found to be contracted (by 2–3 %) in the first and slightly expanded (by 0–1.5 %) in the second interlayer spacing.

This trend in surface relaxation makes the case of Gd(0001) especially interesting. There are two mutually contradictory theoretical results about the relaxation of Gd(0001). One was obtained by Wu *et al.*[9] from a total-energy calculation done with the all-electron local-density full-potential linearized augmented-plane-wave method: this calculation finds that Gd(0001) is relaxed by an outward *expansion* of 6.3% of the first interlayer spacing. The other was obtained by Chen[10] from a total-energy calculation done with local-volume potentials, a method similar to the embedded-atom method: this calculation finds that on Gd(0001) the first interlayer spacing is *contracted* 2.27% and the second interlayer spacing is also contracted 0.92%. Pertinent experimental data for Gd(0001) are not available in the literature at the time of this writing.

We present here the results of a quantitative LEED intensity analysis of a clean Gd(0001) surface. We describe in Sec. II the procedures followed for the growth of high-purity single crystals of Gd and for the preparation of an atomically clean (0001) surface. We then describe in Secs. III and IV the LEED experiment and the analysis of LEED intensities, respectively, and we compare, in Sec. V, our experimental results with the theoretical results mentioned above.

II. SAMPLE AND SURFACE PREPARATION

High-purity gadolinium, obtained from the Ames Laboratory, Iowa State University, was further purified using both zone refining and solid-state electrotransport (SSE). The aim of the zone refining was to reduce the levels of the common metallic impurities (e.g., Fe, W, Al) while

the SSE was used to refine, with respect to the interstitial impurities, O, N, C, and H (Ref. 11). A total of 20 molten zones was passed during zone refining using induction heating with the sample contained in a copper cold boat. After zone refining, the first 15% and the last 45% (in length terms) of the sample were discarded, the remainder being reformed into a sample suitable for SSE. This sample was processed for a total time in excess of 2500 h in an ultrahigh-vacuum environment at temperatures of up to approximately 1100 °C. Crystal growth occurred during the SSE refining as a result of the normal recovery, recrystallization, and grain-growth processes and, possibly, the electromigration of grain boundaries and other crystal defects.[12] The specimen used in this study was cut from the center-anode section of the SSE sample and had a measured resistance ratio of 150.

This specimen was oriented along the ⟨0001⟩ direction by means of Laue diffraction patterns. A platelet was cut perpendicular to the ⟨0001⟩ direction with a slow-speed diamond wheel, and a surface was polished with diamond paste and kerosene to within 0.5° of the basal plane. The final sample had approximate dimensions of $10\times6\times1$ mm^3.

In the experimental chamber the sample was mounted on a sample holder by means of 0.25-μm-thick Ta foil that pressed the sample against a supporting Ta platelet. In the second of the two runs made in this work, the Ta platelet was braized to a short Cu braid which, on the opposite end, was braized to a stainless-steel U tube. A flow of liquid nitrogen through the U tube cooled the sample to about −120 °C.

The sample could be heated by electron bombardment of the back surface through a hole in the supporting Ta platelet. The front surface of the sample was monitored for impurities by Auger electron spectroscopy (AES) with the LEED electron optics used as a retarding field analyzer (RFA). The (doubly differentiated) AES lines of detectable impurities were referred to the Gd AES line at 138 eV as described below.

Carbon was monitored with the ratio $R_C=I_C(272)/I_{Gd}(138)$, where $I_C(272)$ is the intensity of the C AES line at 272 eV and $I_{Gd}(138)$ is the intensity of the Gd AES line at 138 eV. With similar notation, we define $R_O=I_O(512)/I_{Gd}(138)$ for oxygen, $R_{Cl}=I_{Cl}(181)/I_{Gd}(138)$ for chlorine, and $R_{Fe}=I_{Fe}(47)/I_{Gd}(138)$ for iron.[13] The initial values measured on the Gd(0001) surface after attainment of base pressure in the chamber (1×10^{-10} Torr) were $R_C=0.12$, $R_O=0.34$, $R_{Cl}=0.06$, and $R_{Fe}=0.0$. An AES scan taken at this stage is depicted in Fig. 1, curve *a*.

Two runs were made in this study. In the first run the LEED data were collected on the sample at room temperature; in the second run the LEED data were collected on the sample at about −120 °C. Since the sample was exposed to room air between the first and the second run, the surface-cleaning procedures were somewhat different in the two runs. We describe first the (lengthier) procedure followed in the first run.

The surface was subjected to a series of Ar-ion bombardments (2×10^{-5} Torr, 375 V, about 2 μA) for a total of 39 h. These treatments reduced the AES signals of all impurities to the noise level, as shown in Fig. 1, curve *b*. However, after these treatments no LEED pattern was observable: after 1-h anneal at 600 °C, the carbon signal reappeared and a small Fe signal became visible at 47 eV (Fig. 1, curve *c*). In general, Ar-ion bombardments of the hot surface at any temperature between 350 and 1000 °C did not decrease the C signal significantly and, instead, increased the Fe signal very noticeably; see e.g., Fig. 1, curve *d*, recorded after a series of Ar-ion bombardments of the hot surface at 550–600 °C for a total of 16 h ($R_C=0.16$, $R_{Fe}=0.95$). In the course of these treatments, the Gd surface was also tested by LEED, but the LEED patterns were always unsatisfactory, i.e., with broad spots and high background, and they remained so even after several Ar-ion bombardments at elevated temperatures.

After the treatments described above, a satisfactory procedure was found that produced the smallest concentration of impurities *and* a sharp 1×1 LEED with reproducible $I(V)$ spectra. The surface was first bombarded at room temperature with Ar ions for about 25 min, then heated to 1050 °C in 1 min, kept at this temperature for 2 min, and finally allowed to cool rapidly (the temperature dropped to 450 °C in 30 sec and to 350 °C in 60 sec). This procedure produced reproducibly the cleanest surface and the sharpest 1×1 LEED pattern. An AES scan taken after such a treatment is depicted in Fig. 1, curve *e* ($R_C=0.04$, $R_{Fe}=0.02$, $R_{Cl}=0.05$, $R_O=0.0$). This condition is defined as "clean" for the LEED experiments carried out in this work. In this condition the LEED $I(V)$ spectra were always reproducible.

In the second run, when the sample was connected to the stainless-steel U tube, the sequence of treatments needed to produce a clean surface was simpler. After attainment of base pressure the surface appeared cleaner than in the first run (between the first and the second run the sample had been exposed to air only for about 30 h): a short anneal at 500 °C produced an acceptable LEED pattern, but the impurity concentrations were relatively high ($R_C=0.01$, $R_{Fe}=0.32$, $R_{Cl}=0.68$, $R_O=0.27$). Brief Ar-ion bombardments were sufficient to eliminate the O and the Cl impurities and to reduce the C concentration, but the procedure described above (anneal to and quenching from 1050 °C) was necessary to produce good order (sharp 1×1 LEED pattern) and low Fe concentrations (Fig. 1, curve *e*).[14]

III. LEED EXPERIMENT

In general, the LEED patterns from clean Gd(0001) were better (sharper spots, lower background) than those from clean Tb(0001) (Ref. 3). On room-temperature Gd(0001), higher-order LEED spots could be observed above background up to about 350 eV, whereas on cold Gd(0001) (at approximately −120 °C) they could be observed up to more than 500 °C.

Intensity data were collected with a TV-camera-microcomputer system as described elsewhere.[15] The $I(V)$ spectra used in the intensity analysis were 10, 11, 20, 21, and 30 at normal incidence, and 00, 10, 01, $0\bar{1}$, $1\bar{2}$, $\bar{1}\,\bar{1}$, and $0\bar{2}$ at $\theta=7.5°$, $\phi=0°$ (the value $\phi=0$ of the az-

imuth angle means that the parallel component $k_{\parallel}$ of the incident wave vector laid along the $\langle 10 \rangle$ direction in reciprocal space).

The differences between $I(V)$ spectra from clean room-temperature Gd(0001) and $I(V)$ spectra from clean cold (-120°C) Gd(0001) were minimal. The intensity peaks were somewhat sharper (smaller half-width) in the latter spectra, especially at electron energies larger than about 150 eV, as expected, but otherwise the two sets of data were essentially identical. The intensity analysis described below was done with the set collected from the sample at room temperature.

IV. LEED INTENSITY CALCULATIONS AND ANALYSIS

The calculations of LEED intensities were done with the Van Hove–Tong program in the layer-doubling mode.[16] Relativistic phase shifts of Gd were calculated with a program provided by Koelling and Harmon[17] from relativistic charge densities provided by Christensen.[18] Ten phase shifts and 51 beams were used to represent the wave function up to energies of 300 eV by taking into account the presence of the mirror plane in the structure. The inner potential was chosen initially as

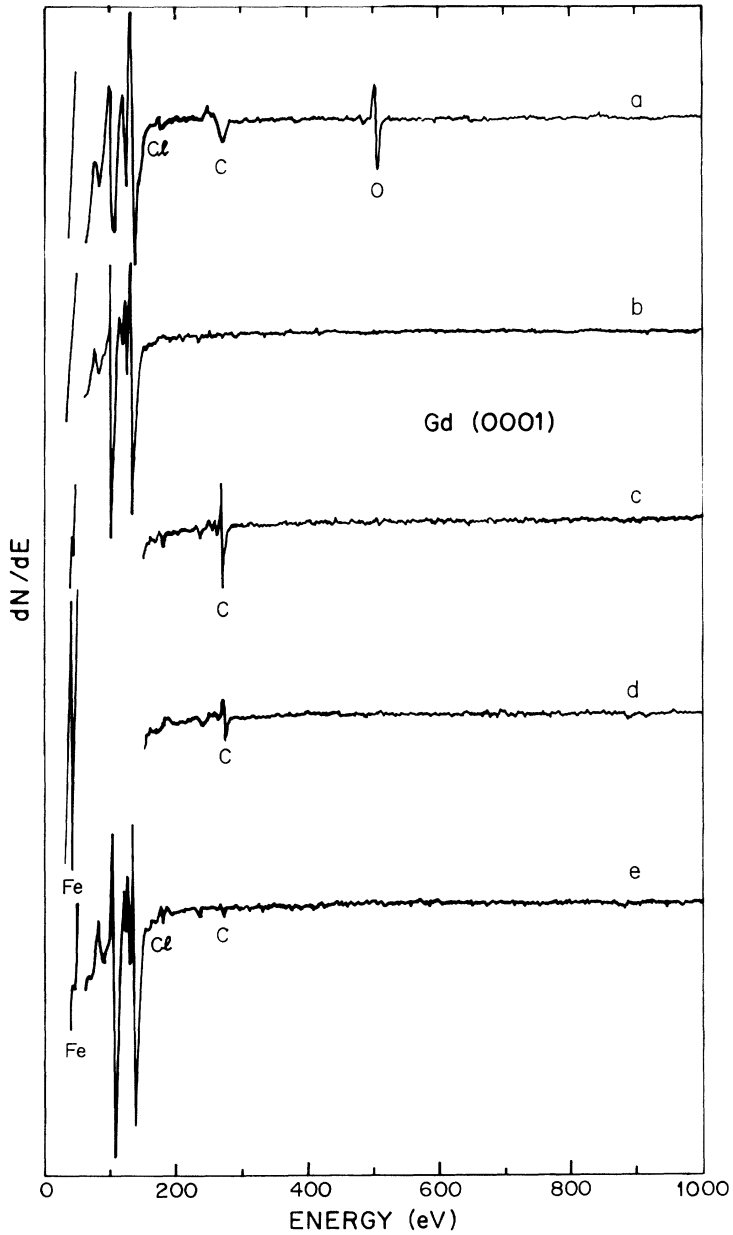

FIG. 1. AES scans of Gd(0001) at different stages of the cleaning process. The settings of the RFA analyzer were the same for all scans, so that the relative intensities of the AES lines can be compared to one another. (a) After attainment of base pressure and before cleaning; (b) after 39-h Ar-ion bombardments; (c) after anneal at 600°C (here the Gd lines between 96 and 160 eV have been omitted); (d) after Ar-ion bombardments of the surface at 550–600°C for 16 h (here the Gd lines between 96 and 160 eV have been omitted); (e) after the final treatment described in the text.

$V_0 = -(10+i4.5)$ eV, but the real part was varied in the course of the analysis in order to match experiment: the final value was $V_0 = -(9+i4.5)$ eV. The atomic vibrations were taken into account with a Debye temperature $\Theta_D = 152$ K. The layer-doubling calculations involved 16 layers in the bulk and 2 layers in the surface. Convergence was achieved after 4 iterations.

The analysis of the normal-incidence data was done in two major steps: first an initial search was made over wide ranges of parameter space and then a refinement was carried out in a narrow region of parameter values around the best fit found in the first step. The evaluation of the fit between theory and experiment was done both visually and by means of three reliability factors, namely, R_{VHT} (Ref. 19), r_{ZJ} (Ref. 20), and R_P (Ref. 21).

All models tested in this analysis were based on bulk-like termination of the hcp structure along the basal plane, but with relaxation of the first (d_{12}) and second (d_{23}) interlayer spacings. The search was done by variation of the *changes* Δd_{12} and Δd_{23} of the two interlayer spacings d_{12} and d_{23}, respectively, with respect to the bulk value 2.845 Å. Initially, only Δd_{12} was varied between -0.2 and $+0.2$ Å. All three R factors pointed toward a minimum in the vicinity of $\Delta d_{12} = -0.1$ Å. The refinement involved variations of Δd_{12} from -0.20 Å to 0.0 in steps of 0.05 Å, together with variations of Δd_{23} from -0.20 to $+0.20$ Å in steps of 0.05 Å.

The parameter values that provided the best fit to the normal-incidence experiment varied somewhat, depending on the reliability factor used, as follows:

minimum $R_{VHT} = 0.231$

for $\Delta d_{12} = -0.105$ Å, $\Delta d_{23} = +0.075$ Å,

minimum $r_{ZJ} = 0.208$

for $\Delta d_{12} = -0.115$ Å, $\Delta d_{23} = +0.065$ Å,

minimum $R_P = 0.256$

for $\Delta d_{12} = -0.085$ Å, $\Delta d_{23} = +0.050$ Å.

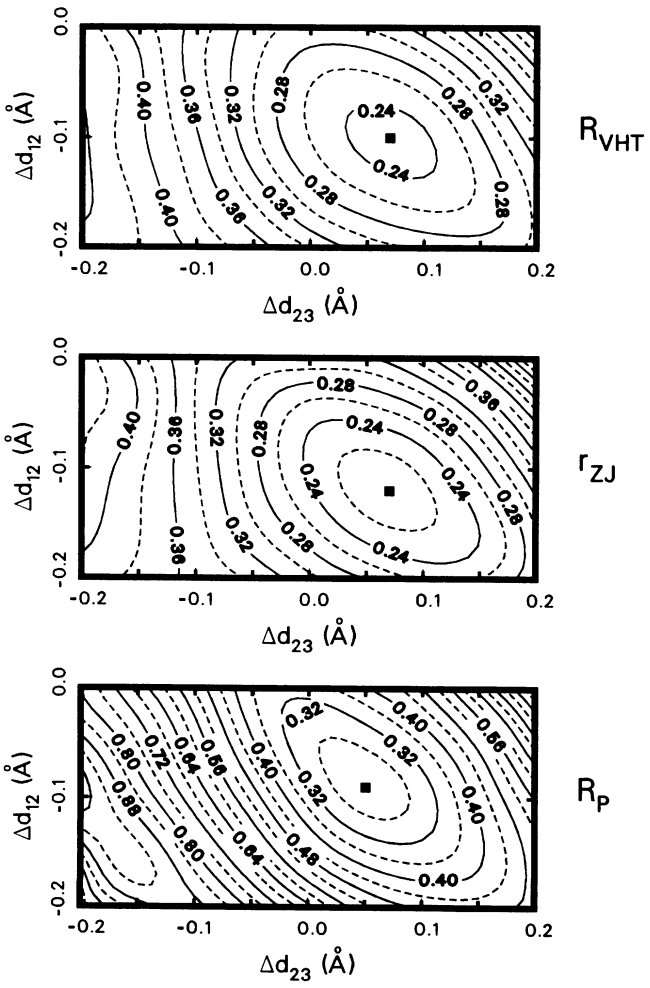

FIG. 2. Contour plots of the Van Hove–Tong R_{VHT}, the Zanazzi-Jona r_{ZJ}, and the Pendry R_P reliability factors for the normal-incidence data from Gd(0001).

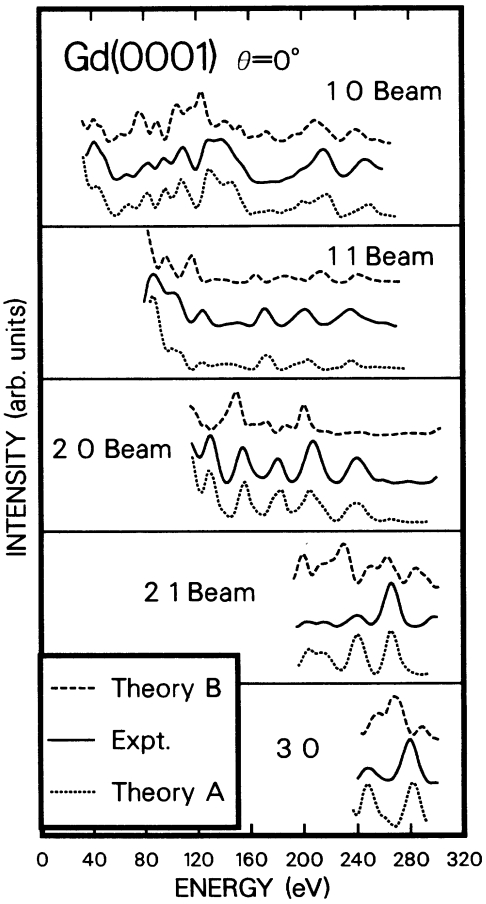

FIG. 3. LEED $I(V)$ spectra for normal incidence on Gd(0001): in each panel the solid curve is experimental, the (dotted) bottom curve (theory A) is calculated for the best-fit model described in the text, and the (dashed) top curve (theory B) is calculated for the model involving 6.3% expansion of the first interlayer spacing.

Contour plots of the three R factors are shown in Fig. 2. Since the differences between the best-fit values given by the three R factors are close to the estimated experimental error of ± 0.03 Å, we quote the final result, for the normal-incidence data, as the average of the above values,

$$\Delta d_{12} = -0.10 \pm 0.03 \text{ Å or } \Delta d_{12}/d_{\text{bulk}} = (-3.5 \pm 1.0)\% ;$$

$$\Delta d_{23} = +0.06 \pm 0.03 \text{ Å or } \Delta d_{23}/d_{\text{bulk}} = (+2.0 \pm 1.0)\% .$$

The $I(V)$ curves calculated with these parameters are drawn dotted (theory A) and compared to experiment (solid curves) in Fig. 3. As the R-factor minima indicate, the agreement between theory and experiment is good.

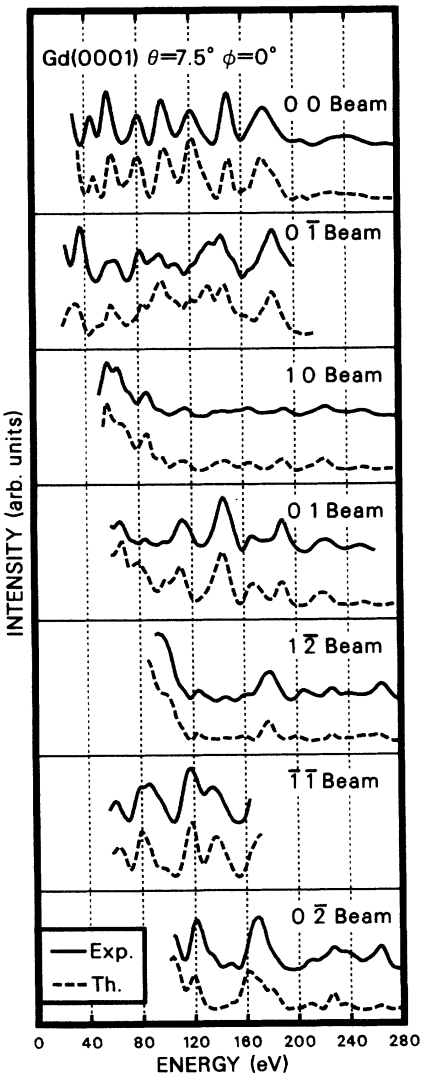

FIG. 4. Experimental (solid) and best-fit calculated (dashed) LEED $I(V)$ spectra for non-normal incidence ($\theta = 7.5°$ $\phi = 0°$) on Gd(0001).

The structure parameters were also tested with the non-normal-incident data set. The calculation done with the above parameters at $\theta = 7.5°, \phi = 0°$ produced the $I(V)$ spectra that are compared to experiment in Fig. 4. The agreement is obviously good, and the three R-factor values are $R_{\text{VHT}} = 0.22$, $r_{\text{ZJ}} = 0.20$, and $R_{\text{P}} = 0.25$.

V. DISCUSSION

The relaxation of Gd(0001) involves a contraction of the first interlayer spacing by 3.5% and an expansion of the second interlayer spacing by 2.0% of the bulk value (2.89 Å). This relaxation follows the trend of surface relaxations measured on other hcp(0001) crystals[22] and is, in particular, very similar to the relaxation found on clean Tb(0001) [$\Delta d_{12}/d_{\text{bulk}} = -3.9\%$ and $\Delta d_{23}/d_{\text{bulk}} = +1.4\%$, $d_{\text{bulk}} = 2.845$ Å (Ref. 3)].

The present result is in fair agreement with Chen's calculations with regard to Δd_{12} (-2.27%), but not with regard to Δd_{23} (-0.92%). It also contrasts strongly with the calculations of Wu and Freeman with regard to Δd_{12} ($+6.3\%$). To test the latter authors's result more directly, we have calculated the $I(V)$ curves expected from a model involving 6.3% expansion of the first interlayer spacing ($\Delta d_{12} = +0.18$ Å), and we have plotted these curves in Fig. 3 (dashed curves, theory B, in each panel). It is obvious that the fit to experiment is noticeably worse than our result—the corresponding R-factor values are $R_{\text{VHT}} = 0.45$, $r_{\text{ZJ}} = 0.54$, and $R_{\text{P}} = 0.73$. We have further optimized the expansion model by keeping $\Delta d_{12}/d_{\text{bulk}} = +6.3\%$ and varying Δd_{23} to minimize the R factors. With this constraint, we find R-factor minima to occur with $\Delta d_{23} = -0.15$ Å or -0.20 Å, but the visual fit to experiment is not much better than that shown in Fig. 3 for $\Delta d_{23} = 0.0$, and the corresponding R factors are $R_{\text{VHT}} = 0.38$, $r_{\text{ZJ}} = 0.40$, and $R_{\text{P}} = 0.52$. Thus, the theoretical prediction[9] of 6.3% expansion of the first interlayer spacing on Gd(0001) is not confirmed.

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