

Unusual Multilayer Surface Alloy: Al(100)- $c(2 \times 2)$ -2Li

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(Received 4 April 2001; published 9 August 2001)

An unusual multilayer surface alloy is formed by adsorption of one monolayer Li on Al(100). It is shown by low energy electron diffraction that the first three layers consist of a mixed Al-Li layer, a pure Al layer, and a second Al-Li layer. Thus the alloy has the same layer stoichiometry as the (100) surface of the metastable Al₃Li bulk alloy. However, the relative orientation of the two mixed layers is the same as that in the Al₃Ti-type structure. These findings are confirmed by total-energy calculations, which lead further to the prediction that the bulk Al₃Li alloy has a faulted, Al₃Ti-type surface.

DOI: 10.1103/PhysRevLett.87.096102

PACS numbers: 68.35.Bs, 61.14.Hg, 68.35.Md

It is well known that the surface properties of binary alloys can exhibit relaxations of both geometry and chemical composition with respect to the bulk. However, the presence of a surface can also lead to more dramatic phenomena, in which unique surface alloys are formed between metals which *do not* form bulk alloys. A prime example of the latter is the formation of surface alloys by adsorption of the alkali metals Na, K, Rb, and Cs on Al surfaces [1]. In the present work we report the occurrence of a uniquely different type of surface alloy, which is formed by two metals, Al and Li, which *do* form bulk alloys, but where the structure of the surface alloy is unknown in the bulk. The result is obtained by analysis of low energy electron diffraction (LEED) data and confirmed by total-energy calculations, which in turn lead to the novel prediction that the surface of a bulk Al₃Li alloy will similarly deviate from the bulk geometry.

Al-Li alloys are of significant technological and fundamental interest because of their unusual mechanical properties and the fact that Li is the only alkali which alloys with aluminum. Al-rich Al-Li alloys are used in the aerospace industry because of their high strength and low density compared to other Al binary alloys [2,3].

The bulk phase diagram for Al-Li contains a single, stable crystalline phase, namely, the AlLi phase with bcc-like NaTl structure. However, a metastable Al₃Li phase is also found, which has an fcc-like Cu₃Au structure. This phase forms as microcrystalline precipitates which can occupy up to 50% of the crystal volume [4]. Al₃Li precipitates are thought to play an important role in establishing the stiffness of Al-rich alloys both by pinning down defects and by their own large Young's modulus. The main features of the experimental phase diagram have been confirmed by a number of theoretical studies. In particular, Freeman and co-workers [5,6] have shown that the Al₃Li alloy is stable at 0 K, but metastable at room temperature.

Previous studies have shown that submonolayer adsorption of Li on close-packed Al surfaces results in the formation of substitutional surface alloys [7–9]. However, it has been an open question as to whether the surface structures

have any relation to bulk Al-Li alloys. For the adsorption of Li on Al(100), it has been established that a $c(2 \times 2)$ -Li structure is formed in which 0.5 ML (monolayer) Li atoms substitute 0.5 ML Al atoms in the first layer [8]. This result has been confirmed by total-energy calculations in the present work and in a separate study [10]. High-resolution core-level spectroscopy (CLS) measurements have shown that adsorption of 1 ML of Li leads to the formation of a three-layer surface alloy [9], containing a mixed Al/Li layer, followed by a pure Al layer, followed by a second mixed Al/Li layer. LEED pattern observations indicate that this phase is also $c(2 \times 2)$, but that the $c(2 \times 2)$ -2Li phase formed by adsorption of 1 ML Li is much less well ordered than the $c(2 \times 2)$ -Li phase formed by adsorption of 0.5 ML Li. Based on the bulk Al-Li phase diagram, it was suggested that the structure of the $c(2 \times 2)$ -2Li phase probably corresponded to the first three layers of the metastable bulk Al₃Li alloy.

In this study we show that a well-ordered $c(2 \times 2)$ -2Li phase can be prepared by adsorption at temperatures in the range 380 to 440 K. A LEED analysis confirms the basic three-layer model suggested by CLS measurements. However, it is found quite unexpectedly that the structure does not correspond to the first three layers of the bulk Al₃Li alloy but rather to the first three layers of the bulk Al₃Ti structure. This conclusion has been confirmed by total-energy calculations, which in turn lead to the prediction of an unexpected surface structure for the bulk Al₃Li alloy. In the following we describe first the LEED experiment and analysis, then the density functional theory (DFT) calculations of total energy.

The Al(100) crystal was cleaned by cycles of Ar⁺ bombardment and annealing to 720 K. Li was deposited onto the crystal by evaporation from a thoroughly degassed SAES source [11]. LEED intensity-energy spectra were measured [12] for the $c(2 \times 2)$ -2Li phase at 100 K and at normal incidence, in the energy range 40–450 eV with a step size of 1 eV. After averaging symmetry-equivalent beams, the data sets contained seven integral-order and five fractional-order symmetry-inequivalent beams. Sets of intensity spectra were measured after adsorption of ~ 1 ML

of Li at temperatures in the range 300–480 K in steps of 20 K. The optimal $c(2 \times 2)$ -2Li structure, as judged by the relative intensity of fractional- and integral-order beams, was found to form in a temperature range between 380 to 440 K.

LEED intensities were calculated using the dynamical theory of LEED [13–16]. Atomic scattering matrices for Al and Li were calculated using up to 18 phase shifts calculated from the muffin-tin band-structure potentials of Moruzzi *et al.* [17], and were renormalized for the effects of thermal vibrations, using atom and layer-dependent root-mean-square (rms) isotropic vibrational amplitudes. The complex electron self-energy $\Sigma = V_0 + iV_{im}$ was taken to be independent of energy.

Refinement [7,14] of all structural and nonstructural parameters in the first four surface layers was performed for two different, three-layer, surface alloy structures with Cu_3Au -type and Al_3Ti -type geometries, respectively. The Al_3Ti -type surface structure, as sketched in Fig. 1 together with the corresponding bulk Al_3Ti structure, gave a significantly better agreement between experimental and calculated intensity spectra, yielding an R factor [7] of $R = 0.053$ as compared to $R = 0.135$ for the Cu_3Au -type structure expected for bulk Al_3Li . The detailed results of the structure determination are given in Table I. Plots of a subset of the experimental intensity spectra and spectra calculated for the optimum parameter values given in Table I are shown in Fig. 2.

The degree of ordering of the alloy structure was investigated by carrying out analyses of LEED intensities measured for different deposition temperatures. Intensities were calculated using the averaged t -matrix approximation [18,19] for a structure with a perfect $c(2 \times 2)$ -Li first layer, but with different Li concentrations in the second and deeper layers. It was found that the LEED intensities were incompatible with nonzero concentrations of Li in the 2nd layer for all deposition temperatures between 300 to 450 K. However the analyses indicated that the Li concentration in the third layer increases with deposition temperature, reaching 0.5 ML at deposition temperatures above 380 K, where the $c(2 \times 2)$ -Li structure appears to be perfectly developed. The possibility of randomly distributed Li in the fourth layer was also investigated, but it was found that nonzero Li concentrations resulted in an increase of the R factor. Finally, a structure in which both the third and the fifth layers consisted of mixed $c(2 \times 2)$ -Al/Li layers was also investigated but the intensities were not sensitive enough to the presence of Li in the fifth layer to draw firm conclusions.

Following the LEED analysis, we performed *ab initio* total-energy DFT calculations [20] with a plane-wave basis set and norm-conserving pseudopotentials [21] to determine the structure of lowest energy. This involved calculating the total energies of Al(100) slabs consisting of nine layers, where the first and third (and fifth) layers had a mixed, Al(100)- $c(2 \times 2)$ -Li structure. A cutoff energy of 13 Ry and 36 k -points in the irreducible wedge

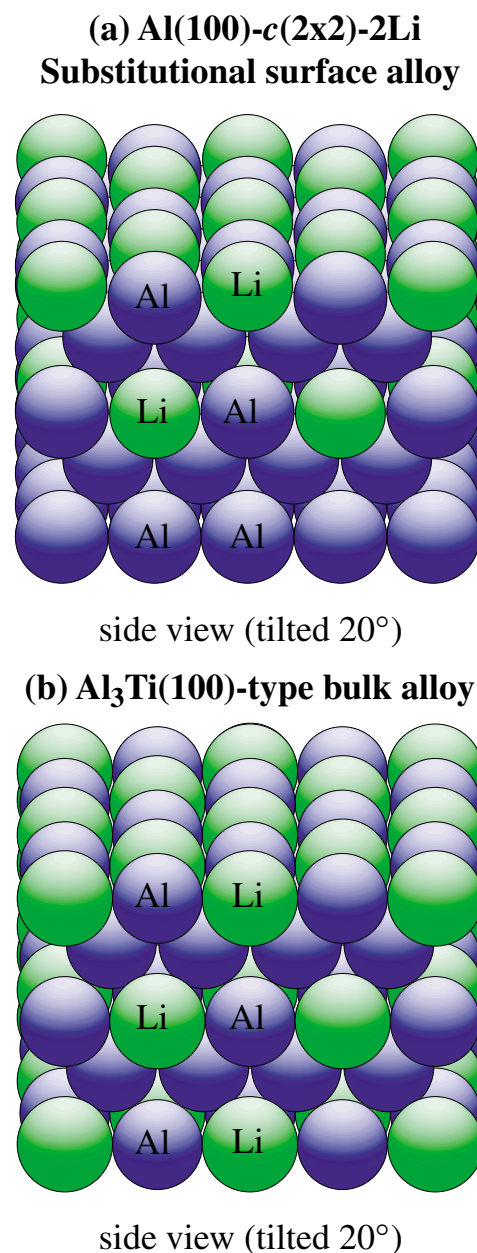


FIG. 1 (color). (a) Hard-sphere model of the Al(100)- $c(2 \times 2)$ -2Li structure, shown as a central projection on the (110) plane, in a side view tilted by 20° with respect to the plane of the paper. Li atoms are shown in green; Al atoms are shown in blue. (b) Corresponding model of a hypothetical Al_3Ti -type bulk alloy. Note that in the Cu_3Au -type structure of bulk Al_3Li , Li atoms in successive mixed layers lie directly beneath each other, rather than in the staggered arrangement of the Al_3Ti -type structure. In other words, the Cu_3Au -type structure is obtained from (b) by switching the positions of Al and Li atoms in the second (and fourth, etc.) mixed Al/Li layer.

of the Brillouin zone (distributed in accordance with the Monkhorst-Pack scheme [22]) was found sufficient for convergence of the total energy. The exchange-correlation functional was described by a generalized gradient approximation [23]. For the Al_3Ti and Cu_3Au structural models considered here, the total energy was

TABLE I. Structural parameters determined by LEED and DFT for the three-layer Al(100)- $c(2 \times 2)$ -2Li phase. DFT calculations for a hypothetical five-layer Al(100)- $c(2 \times 2)$ -3Li phase are also included. Layers a and b of the stacking sequence are both $c(2 \times 2)$ substitutional Al/Li layers. However in the b layers the Al and Li atoms have switched places compared to the a layers. In each sequence, the mixed a or b layers are separated by a pure, planar Al layer. Δd_1 , Δd_3 , and Δd_5 are the vertical separations between Li and Al atoms in mixed and rumpled first, third, and fifth layers, where positive values correspond to Li atom positions being closer to the surface than Al. d_{ij} are the vertical separations between the outer surfaces of the i th and j th layers.

Method: Structure: Stacking sequence	Density functional theory calculations						
	LEED Al ₃ Ti ba	Al ₃ Ti ba	Cu ₃ Au aa	Al ₃ Ti/Cu ₃ Au baa	Al ₃ Ti bab	Cu ₃ Au/Al ₃ Ti aab	Cu ₃ Au aaa
Parameter							
Δd_1	$0.38 \pm 0.04 \text{ \AA}$	0.322 \AA	0.241 \AA	0.312 \AA	0.312 \AA	0.248 \AA	0.225 \AA
d_{12}	$1.82 \pm 0.01 \text{ \AA}$	1.85 \AA	1.89 \AA	1.84 \AA	1.84 \AA	1.89 \AA	1.89 \AA
d_{23}	$1.95 \pm 0.02 \text{ \AA}$	1.98 \AA	2.01 \AA	1.97 \AA	1.97 \AA	2.00 \AA	2.00 \AA
Δd_3	$-0.04 \pm 0.04 \text{ \AA}$	0.007 \AA	0.012 \AA	-0.199 \AA	0.029 \AA	0.038 \AA	-0.014 \AA
d_{34}	$2.02 \pm 0.02 \text{ \AA}$	1.98 \AA	2.01 \AA	2.00 \AA	2.00 \AA	2.01 \AA	2.00 \AA
Δd_5				0.091 \AA	-0.029 \AA	-0.002 \AA	0.017 \AA
E_{ads}		-4.56 eV	-4.45 eV	-6.79 eV	-6.65 eV	-6.64 eV	-6.66 eV

optimized with respect to relaxations of all parameters allowed within the $c(2 \times 2)$ unit cell in a fourfold rotational and mirror symmetry, in accordance with the symmetry of the observed LEED pattern.

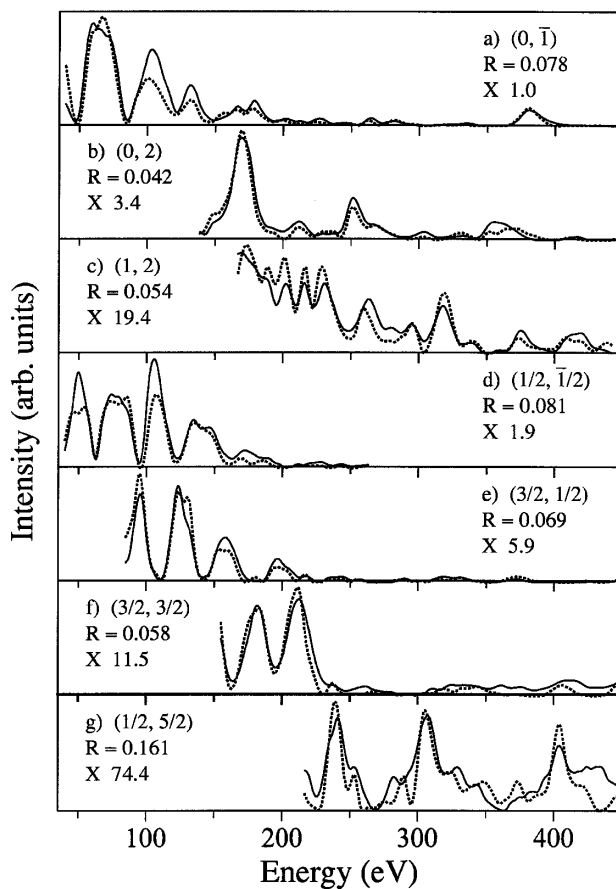


FIG. 2. Comparison of experimental (solid lines) and calculated (dotted lines) intensity-energy spectra for Al(100)- $c(2 \times 2)$ -2Li at $\theta = 0^\circ$ for three integral-order and four fractional-order beams, (a)–(g). The beam hk indices, R factors, and scale factors are shown in each panel. The calculated spectra were obtained using the best-fit parameter values given in Table I.

For a three-layer surface alloy, the DFT calculations confirm the LEED results, in that the Al₃Ti-type structure is found to be more stable than the Cu₃Au-type structure by ~ 0.1 eV per unit cell. The structural parameters found by DFT calculations agree quantitatively with the LEED results, as can be seen from the comparison given in Table I. It is interesting to note that the Al₃Ti-type structure is energetically favored regardless of the extent to which Li atoms in the first layer are relaxed out of the plane. It seems likely therefore that the preference for the Al₃Ti-type surface has to do with the nature of the Al-Li bonding rather than being a consequence of surface relaxation. It has been shown previously that Al-Al bonds in AlLi and Al₃Li alloys are strengthened by donation of a Li valence electron [24,25]. The substitutional Li atoms in the first layer of an Al₃Ti-type or Cu₃Au-type structure have only eight nearest-neighbor Al atoms to receive their valence charge, as opposed to twelve nearest neighbors in the bulk. However, in the Al₃Ti-type structure, these Li atoms can donate charge to a next-nearest-neighbor Al atom in the third layer that is not present in the Cu₃Au-type structure. A further strengthening of Al-Al bonds in this way is suggested by an additional pileup of charge found in electron density projections of the third layer in the Al₃Ti-type structure.

In view of the agreement between the LEED and DFT studies of the three-layer surface alloy, it was of obvious interest to investigate the further development of the structure with depth. DFT calculations for Al(100)- $c(2 \times 2)$ -3Li show that this five-layer alloy reverts to a Cu₃Au stacking, but preserves the Al₃Ti structure at the surface. The stacking sequence of the mixed Al/Li layers is thus baa , as opposed to aaa for Al₃Li. The adsorption energies and structural parameters of the four possible stacking sequences of mixed $c(2 \times 2)$ layers are given in Table I. Finally, it is noted that further DFT calculations of the bulk Al₃Li alloy for structures of the Al₃Ti type and Cu₃Au type confirm the conclusions of Guo *et al.* [25], that the Cu₃Au-type structure is energetically favored. The energies of formation per atom [25] are found to be

$\Delta H_f = -0.098$ eV for the Cu_3Au type and $\Delta H_f = -0.082$ eV for the Al_3Ti type. However, the *surface* structure of Al_3Li is predicted to have a stacking fault, such that it consists of a three-layer Al_3Ti -type structure on a Cu_3Au -type bulk. A surface three-layer Al_3Ti -type structure is favored by about 0.1 eV per unit cell as compared to a pure Cu_3Au -type crystal.

At the present time the novel theoretical predictions for the surface structure of bulk Al_3Li and the structure of a five-layer surface alloy await experimental confirmation. In the case of the surface alloy, as noted above, test calculations indicated that a LEED structure analysis would be marginal because of lack of sensitivity at this depth, unless a significant rumpling of the third layer occurred, as predicted (see Table I). However, attempts to prepare such an alloy to date indicate that diffusion of Li into the bulk occurs rather than growth of a third mixed Al/Li layer.

Finally it is interesting to speculate if the Al_3Ti -type surface alloy found here for the Al(100) surface is relevant to the structures formed by adsorption of Li on other Al surfaces. In this regard we note that the structure of the Al(110)- $c(2 \times 2)$ -Li phase [26] is in fact very similar to the first layer of Al_3Ti (110), and that alloy formation in deeper layers has also been observed by CLS.

Support of this work by the Danish and Swedish Natural Science Research Councils is gratefully acknowledged.

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