Interrelation of work function and surface stability: the case of BaAl₄

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The relationship between the work function (Φ) and the surface stability of compounds is, to our knowledge, unknown, but very important for applications such as organic light-emitting diodes. This relation is studied using first-principles calculations on various surfaces of BaAl₄. The most stable surface [Ba terminated (001)] has the lowest Φ (1.95 eV), which is lower than that of any elemental metal including Ba. Adding barium to this surface neither increases its stability nor lowers its work function. BaAl₄ is also strongly bound. These results run counter to the common perception that stability and a low Φ are incompatible. Furthermore, a large anisotropy and a stable low-work-function surface are predicted for intermetallic compounds with polar surfaces.

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I. Introduction

The long-standing problem of the precise relationship between the work function (Φ) and the stability of metals has become pressing with the increased application of electron-emitting materials in technology. Two examples are vacuum electronic devices like cathode-ray tubes (CRTs) and cathodes for organic light-emitting diodes (OLEDs). In CRTs, a thin layer of a low-Φ metal is often present on top of a cathode made from a structurally stable material to enhance its electron-emitting properties. Electron injection into OLEDs strongly depends on the cathode work function, while the lifetime of the device can be limited by the stability of the cathode material. OLEDs with an alloy interface between the cathode and the polymer have been found to be superior, in terms of lifetime and luminosity, to those with single-element cathodes. Thus the relationship between Φ and stability is crucial. However, it is poorly understood, especially for more complex metals.

The general rule for elements is that a low work function and high stability are incompatible: the element with the lowest work function, cesium (Φ = 2.14 eV), is highly reactive and has a low melting temperature. Noble metals (silver/gold/platinum) on the other hand are hardest to oxidize, but their Φ is at least twice as large (4.25/5.1/5.65 eV). It is generally believed that this must always be the case, i.e., that a low Φ implies loosely bound electrons that easily mediate reactions. The work function surface anisotropy, however, can be quite large: for tungsten, it is of the order of 1 eV. The anisotropy was already theoretically addressed by Smoluchowski. According to his model, at a “more open” surface, relaxation of the electrons “smoothes” the surface charge. A dipole moment is built up that lowers Φ. This is schematically shown in Fig. 1. Although the work function is lowered for a more-open surface, the surface energy increases and stable, low-work-function surfaces are forbidden by the model. Hardly any extensions to the model have been suggested since, certainly not for more complex metals. Experimental results for transition metal alloys suggest the so-called alloy effect which implies that the stability and Φ of alloys interpolate between those of the constituting elements. As a consequence, it is believed that stable, low-work-function surfaces are not possible for more complex metals either.

Nevertheless, the work function and stability of compounds mainly constitute a terra incognita. In this paper, the relationship between Φ and stability of compounds is studied for the first time by calculating ab initio the structural relaxation, work function and surface energy of various surfaces of BaAl₄. The motivation to study the BaAl₄ system was the successful use of Ba-Al-alloy cathodes in OLEDs and the high melting point of this compound (> 1000°C). In the Ba-Al phase diagram the melting point of BaAl₄ is the highest, much higher than those of the constituents, which indicates a strongly bound structure. Moreover, we show that the work function for one of the crystal surfaces is very low.

II. Ab Initio Calculations

The BaAl₄ crystal structure is depicted in Fig. 2. It is body-centered tetragonal, with alternately three aluminum layers (1Al, 2Al and 3Al) and one barium layer.
(1Ba) in the [001] direction. Both Al and Ba atoms are located approximately according to their elemental crystal structures (bcc and fcc, respectively). The (100) surface is stoichiometric and there are four (001) surfaces. They are constructed by cutting the bulk above the accordingly labeled layers in Fig. 2. Two other (001) surfaces are also considered: “2Ba” (one bcc barium layer added to 1Ba) and “3Ba” (half a barium layer removed from 1Ba).

From bulk calculations we find that \( a = 4.56 \) Å, that \( c = 11.39 \) Å, and that the remaining free parameter in the structure, the height of the third aluminum layer, is 0.381 \( \cdot c \). These values compare very well (deviations \( \approx 1\% \)) with those obtained experimentally. The bulk density of states (DOS) shows a quasi-gap just below the Fermi level, in accordance with the previously calculated DOS of BaAl\(_4\) and other isoelectronic compounds with the same structure. The valence electrons are mainly located on Al atoms. The binding energy (\( E_{\text{bind}} \)) is 1.42 eV/F.U. with respect to the elemental bulk metals. Together with the quasi-gap, it hints at BaAl\(_4\)’s stability.

The first-principles calculations were carried out using density functional theory (DFT) in the local density approximation (LDA)\(^{15,16}\) with generalized gradient corrections (GGA)\(^{17}\). We used the total energy and molecular dynamics program called VASP (Vienna Ab-initio Simulation Package)\(^{18,19}\) which has the projector-augmented-wave method (PAW)\(^{20,21}\) implemented. Nonlinear core corrections\(^{22}\) were applied for both barium and aluminum. A semi-core of Ba 5s and 5p electrons was included. The Kohn-Sham orbitals were expanded in plane waves with cutoffs of 18 Ry. The Brillouin zones for the (100) and (001) surface calculations were sampled with \( 1 \times 16 \times 8 \) and \( 12 \times 12 \times 1 \) Monkhorst-Pack\(^{22}\) \( k \) point grids, respectively, resulting in eight and 21 \( k \) points, respectively, in their irreducible parts. The (periodically repeated) unit cell for the (100) surface calculation contained a slab with a thickness of seven bulk unit cells and 16 Å vacuum. The supercells for the (001) surface calculations contained slabs with thicknesses of six formula units (F.U.) and 20 Å vacuum.

### III. Work Function

The work function is defined as the amount of energy it takes to extract electrons from a metal, \textit{i.e.}, bring them from the Fermi level to the vacuum. At locations that are microscopically far from the material, but macroscopically near it, \( \Phi \) is surface dependent. The work function at large distance is then an average over the various surfaces. The work function of a surface is calculated by constructing a supercell with a slab of material, with only this surface, and vacuum. Fig. 3 illustrates this using the (001) Ba terminated surface. About 10 Å empty space suffices for the electrostatic potential\(^{25}\) to converge to its vacuum value (\( V_{\text{vac}} \)). A thick slab, however, is required for the Fermi level (\( E_F \)) to be accurate. A more efficient method is to link the surface calculation to a bulk one where \( E_F \) is very accurate. The average potential in the bulk \( (\langle V \rangle_{\text{bulk}}) \) is set equal to the average potential in the middle of the slab. Accuracies of a few hundredths of an eV can thus be achieved with only six to eight bulk unit cells, depending on direction.\(^{27}\) The work function of the 1Ba surface is 1.95 eV.

The work functions of the other BaAl\(_4\) surfaces are calculated analogously. That of the (100) surface is reduced even more to a surprisingly low value of

![Image](https://via.placeholder.com/150)

**FIG. 2:** Body centered tetragonal unit cell of BaAl\(_4\) containing 2 formula units. The labels refer to the layer and atom type. 1Al and 3Al atoms are equivalent in the bulk.

**FIG. 3:** The BaAl\(_4\) (001) 1Ba surface. Laterally averaged charge density (\( \rho \) solid line, arbitrary units) and (electrostatic) potential (\( V \) dashed line, eV relative to \( E_F \)) as function of position perpendicular to the surface (\( z \)). The positions of Ba and Al layers are indicated with light and dark spheres, respectively. At \(-5.12\) eV is the average bulk potential and at \(2.79\) eV the highest potential in the bulk.\(^{26}\) The work function is 1.95 eV.
1.95 eV. This is below the $\Phi$ of any element. An additional layer of barium (thus forming the 2Ba surface) increases $\Phi$ (2.13 eV) again. Experimental bulk values for Al (4.2 eV) and Ba (2.32 eV) are plotted for reference. These compare favorably with calculated work functions of bcc-barium [2.36 eV (100) and 2.27 eV (111)] and fcc-aluminum [4.34 eV (100) and 4.17 eV (111)].

The huge (> 2 eV) variation in the (001) surface work function can be (qualitatively) explained from the difference in the atomic electronegativities. Ba is less electronegative (0.9) than Al (1.5) affecting charge transfer from barium to aluminum. The resulting surface dipole moment decreases the work function of the Ba surface to zero under the elemental barium bulk value and increases $\Phi$ of the Al surfaces considerably. The dependence of $\Phi$ on Al coverage of the 1Ba surface can be understood if one realizes that the 1Al and 3Al surfaces are more open than the 2Al surface. According to the Smoluchowski model, $\Phi$ must then be lowered. The decrease in $\Phi$ during relaxation of the (100) surface can also be understood by combining charge transfer with Smoluchowski smoothing. The barium atoms at the surface move out (≈ 0.1 Å), as they favor an environment with a lower charge density, while the aluminum atoms at the surface tend to get closer together, as they favor an environment of a high charge density. We conclude that a monolayer coverage yields an extreme work function.

**IV. Surface Energy**

The (relative) stability of a surface is determined by the difference in surface energy ($\gamma$) between two surfaces. The surface energy is calculated as the energy of a slab with only this surface minus the energy of the bulk equivalent (formed by merging the periodically repeated slabs together), divided by two times the surface area, because a slab has two sides. This method was used for the (100) and (001) $\frac{1}{2}$Ba surfaces. Slabs for the other (001) surfaces are non-stoichiometric and so there is no equivalent bulk. Calculating $\gamma$ now requires reservoirs of Ba and Al. Assuming thermodynamic equilibrium, the chemical potential of the aluminum ($\mu_{\text{Al}}$) and that of the barium ($\mu_{\text{Ba}}$) reservoir are linked to the total energy per F.U. of BaAl$_4$ ($E_{\text{bulk}}$):

$$E_{\text{bulk}} = 4 \cdot \mu_{\text{Al}} + \mu_{\text{Ba}}. \hspace{1cm} (1)$$

The energy of, for example, the 1Ba surface, as a function of $\mu_{\text{Ba}}$, follows from the total energy of a slab with these surfaces exclusively ($E_{1\text{Ba}}$):

$$\gamma^{1\text{Ba}}(\mu_{\text{Ba}}) = \left[E_{1\text{Ba}} - \# \text{F.U.} \cdot E_{\text{bulk}} - \mu_{\text{Ba}}\right] / 2A_{\text{S}}, \hspace{1cm} (2)$$

where $A_{\text{S}}$ is the surface area.

![Figure 4: Work functions (eV) of the BaAl$_4$ (001) surfaces. Experimental bulk values for barium and aluminum are indicated at the borders. Lines connect the data points. $\Phi$ for the (100) surface before and after relaxation is inserted. (The dotted line is $V_{\text{max}}$.)](image1)

![Figure 5: Surface energies (eV/nm$^2$) for the BaAl$_4$ surfaces as function of the barium chemical potential (eV). The potential ranges from the value for Al bulk to that of Ba bulk. The difference is the binding energy of BaAl$_4$ (equation 4 has been used). For the (100) surface the effect of relaxation is indicated. The (001) 1Ba surface is the most stable.](image2)
aluminum is (partially) ionized.

V. Conclusions.

As both the low $\Phi$ of the 1Ba surface and its stability followed from Ba's lower electronegativity, we come to a remarkable prediction: For an intermetallic compound with polar surfaces, like BaAl$_4$, the most stable surface has the lowest work function and relaxation can only decrease it further.

To summarize, we used first-principles calculations on various surfaces of BaAl$_4$ to study the interrelation of work function and stability. The bulk work function of BaAl$_4$ is 2.79 eV, its anisotropy (1.5 eV) is huge, and the most stable surface (Ba terminated 001) has the lowest $\Phi$ (1.95 eV), which is even lower than that of pure Ba. Adding barium to this surface neither increases its work function nor lowers its work function. The binding energy of 1.42 eV/F.U., the quasi-gap in the DOS, and its melting temperature of over 1000 °C indicate BaAl$_4$'s stability. These results contradict the common perception that stability and a low $\Phi$ are incompatible. They also run counter to the effect that alloy work functions are in between those of the constituting elements. Its stable, very-low-$\Phi$ surface and the stable structure probably make BaAl$_4$ a good electron-emitting material. Furthermore, a stable low-work-function surface promises to be general for intermetallic compounds with polar surfaces.

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