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Brief Reports

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Structural stabilities of layered materials: Pt-Ta

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We suggest that metal multilayer systems can be fruitfully modeled by crystalline-layer-type compounds. As an example we have performed first-principles local-density calculations on the platinum-tantalum system for two compounds, PtTa and Pt_2Ta. The crystal structures considered were CsCl, CuAuI, $MoSi_2$, and $MoPt_2$. These structures may be viewed as stackings of low-index planes of fcc or bcc crystals and may be transformed from one to another by a tetragonal distortion. In contrast, epitaxial growth often involves stackings of close-packed layers and, in the case of the bcc structure, the low-index (100) and close-packed (110) stackings are connected by an orthorhombic distortion. Total energies have been calculated and from these interface energies defined. Tracing the total energies over the above-mentioned distortions has yielded results consistent with known phase-diagram behavior and has suggested that Pt adsorbed on Ta(110) is locally stable although globally unstable.

It has become an increasingly common practice to lay one metal down epitaxially on a single-crystal substrate of another material or to construct a multilayer material. Usually close-packed atomic layers are involved in the stacking. There are also many stable crystal structures[1] which involve atomic layers but these layers are, most often, not the most close packed. This allows more unlike closest-neighboring atom pairs than does the stacking of close-packed layers, and the bonding of such pairs generally enhances the energetics of compound formation. It is the purpose of the present report to explore the heat of formation of a compound as one structure, with such stackings, is distorted into another. This will be done with bulk-metal, total-energy energy-band calculations. The Ta-Pt system will be considered because of the experimental interest[2] in it at our institution and because such layered structures compete to be the stable phases in the bulk. For the case of Ta-Pt, we will see indications that close-packed stacking is locally stable, though globally unstable, with respect to non-close-packed stackings.

It is possible to relate the energetics of the above-mentioned cases to one another, at least crudely. Consider a substrate of substance B, upon which a thick layer of substance A has been laid, in atomic register. Using the elemental solids as reference materials, the heat of adsorbing such a layer is

$$\Delta H = \gamma_A - \gamma_B + 2\xi + \Delta H_{\mathrm{str}} , \qquad (1)$$

where γ_A is the surface energy gained and γ_B that lost by covering. ΔH_{str} is the structural energy cost, if any, in preparing system A to be of the same structure and lattice constant as B and 2ξ is the interface energy, the factor of 2 being included so that its definition is similar to that of surface energies. There is some ambiguity in the assignment of the energy contributions, associated with atoms "in" the interface, between ξ and ΔH_{str}. These may be made as a matter of convenience. Equation (1) may be modified for the case of a multilayer material, with thick layers, by dropping the γ terms and multiplying the ξ term by another factor of 2 since there are two interfaces in a multilayer's unit cell. In the limit of thin adlayers or thin-layered multilayers one might drop ΔH_{str} from the equation, thus incorporating any "structural" energy effects into ξ. The present results will be utilized in preliminary estimates of ξ.

The self-consistent, scalar relativistic, linearized augmented Slater-type orbital (LASTO) method[3] has been employed to obtain total energies for Pt_2Ta (and PtTa) in the $MoSi_2$ (and CsCl) structure which is a 2:1 (and 1:1) stacking of (100) bcc planes of atoms. Local-density, muffin-tin potentials were used.

Sufficiently large sets of special k points were used in order to provide convergence in the crystal total energies as has been documented elsewhere for the elemental $5d$ metals[4] and some of their compounds.[5] For example, 42 special k points were used here for the $MoSi_2$ structure and 69 for the $MoPt_2$ structure. The resulting total energies lead to good heats of formation[5,6] for the ordered alloys and the correct assignment of ground-state phases among competing phases of the same and of different alloy composition—providing that the phases in question are well packed with reasonably high atomic site symmetries (otherwise the muffin-tin potentials do not suffice). Lattice constants of the phases were chosen so that Pt and Ta have atomic volumes consistent with the observed Pt-rich Pt-Ta phases and the muffin-tin sphere radii were assigned so that the spheres did not overlap. The previous calculations suggest that the present results are accurate, granted any limitations in the local-density approximation.

By an orthorhombic distortion the $MoSi_2$ structure may be turned into a (110) stacking of an fcc structure, i.e., the $MoPt_2$ structure, as is illustrated in Fig. 1 and the same distortion takes CsCl into the CuAuI structure. A different distortion, employing rotated coordinates as is illustrated in Fig. 2, takes the least-close-packed (100) stacking of the bcc lattice into the close-packed (110) stacking of the same lattice. (It should be noted that the interlayer spacing, the δz of Fig. 1, of the 2:1 compound will not be exactly one-third of the c-axis dimension z due to the fact that we are stacking different sorts of atoms in different layers. Deviation from the correct δz value corresponds to an optical phonon. Thus the value of $\delta z/z$ is of energetic significance and has been determined variationally in the course of the calculation.) .There is no single path for taking the $MoSi_2$ (or CsCl) structure into one of the others. On going from $MoSi_2$ to $MoPt_2$, the ratio z/x (of Fig. 1) was held fixed which corresponds to maintaining the square symmetry of the (010) planes of Fig. 1. An analogous choice of paths does not appear available on going from $MoSi_2$ to the (110) stacking so, instead, y (of Fig. 2), that is the (010) plane separation, was held fixed. In this sense, the path of least atomic motion was taken between the two structures.

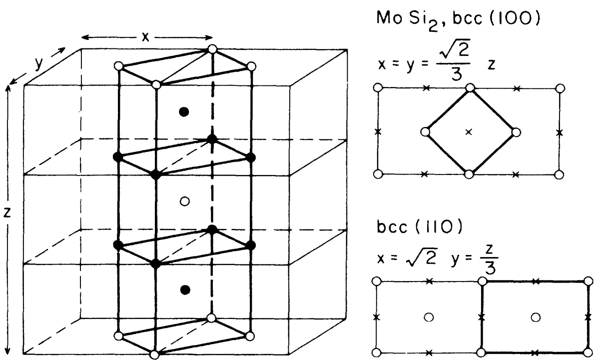

FIG. 2. To the left: a unit cell of the $MoSi_2$ structure inside a larger cell with rotated axes with a view of that cell, as seen from above, being shown to the upper right. The distortion of the larger unit cell which takes the *abb* stacking of (100) bcc planes in the $MoSi_2$ structure into an *abb* stacking of close-packed (110) layers of the bcc structure is shown in the lower right. A similar distortion of *ab* stackings takes the CsCl structure into close-packed (110) stacking.

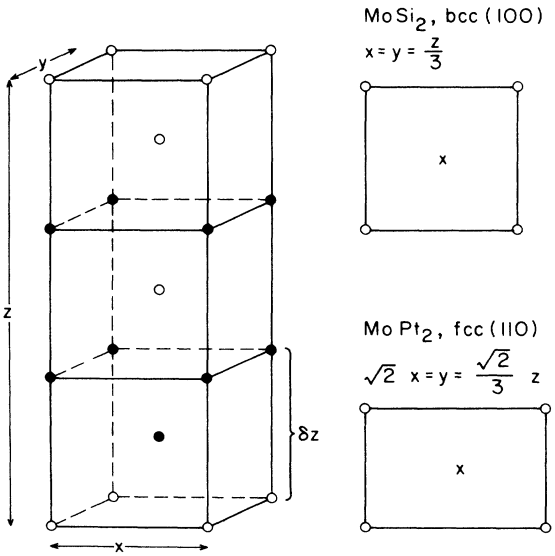

FIG. 1. A unit cell of the $MoSi_2$ structure, with its *abb* stacking of bcc (100) planes, is displayed to the left and a view of this cell, from the top, is shown in the upper right. The distortion which takes this structure into the $MoPt_2$ structure, with its stacking of fcc (110) planes, is indicated at the lower right. The same distortion takes the CsCl into the cubic CuAuI structure.

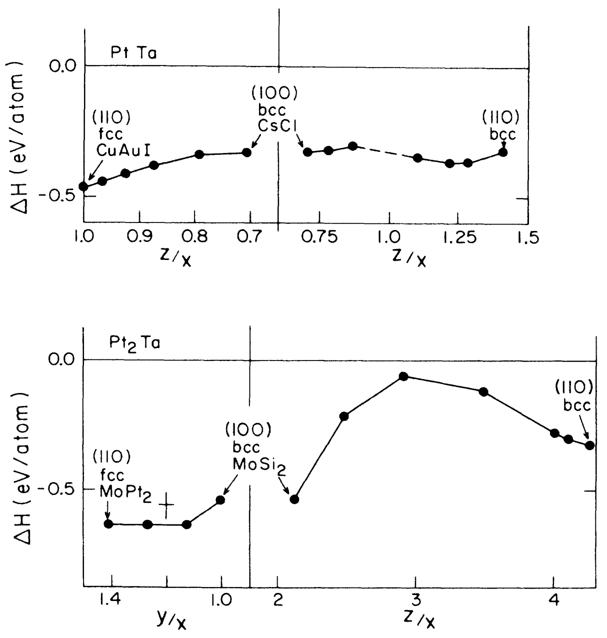

FIG. 3. Heats of formation of PtTa and Pt_2Ta for distortions off the CsCl and $MoSi_2$ structures, respectively. The left-hand panels follow the distortion of these structures into their fcc, cubic CuAuI and $MoPt_2$, structures with x, y, and z defined in Fig. 1. The right-hand panels take the CsCl and $MoSi_2$ structures with their (100) stackings into the close-packed (110) stacks. Here x and z have the meanings defined in Fig. 2.

The calculated heats of formation for PtTa and Pt_2Ta in their various distortions, are plotted in Fig. 3. Consider, first, the bcc↔fcc transitions to the left-hand side of the figure. In both cases the fcc lattice is of lower energy[7] as is expected. There are no barriers to taking the systems from the bcc to their fcc counterparts. This is not the case for the close-packed (110) stackings of the bcc lattice for, though they lie higher in energy, there are barriers to going over to (100) stacking, thus the close-packed stacking is locally, though not globally, stable. [The Pt-Ta calculations have a minimum at $(z/y)\sim 1.25$, indicating a modest distortion of the (110) stacking of the 1:1 compound.]

One can use the (110) results to make estimates of 2ξ by attributing the entire heat of formation of the compound to be the heat of the pair of interfaces making up the unit cell. This leads to values $-\frac{1}{3}$ and $-\frac{1}{2}$ eV per atom in a plane for the 1:1 and 2:1 stacking, respectively. Clearly these layers are too close for the estimate of 2ξ to be taken too seriously but the results are of the order, though somewhat smaller than an estimate based on photoemission data of the heat of adsorbing Pt on Ta. This estimate[2] employs a scheme[8] of Oelhafen's which makes use of the observed shift in the center of gravity of the occupied conduction bands plus a reference level shift based on observed core-level shifts. No proper derivation has been given for this scheme and it would appear to be, at best, semiquantitative, but it does have the virtue of relying entirely on experimentally observable quantities.

We believe that local-density calculations, of the class described here, have considerable promise providing that sufficient care is taken, e.g., that muffin-tin potentials are replaced by full potentials when necessary. Given slab calculations with adsorbed surface layers as well as bulk calculations with unit cells having thicker multilayers, it should be possible to disentangle the various contributions to Eq. (1). The present model calculations provide a first estimate of this. It is also of interest to follow the energetics of a crystal as it distorts. The CuAuI↔CsCl distortion has been considered in a number of papers while the (100)↔(110) bcc distortion has been considered for the first time here. The results obtained for Pt-Ta suggest that the stacking of close-packed atomic layers may well be metastable; that is, locally stable though globally unstable. This issue has implications for the growing activity in the production and utilization of multilayer materials and deserves further investigation.

ACKNOWLEDGMENT

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[1] For example, the CsCl, $MoSi_2$, γ-CuTi, and Al_3Os_2 crystal structures involve *ab*, *abb*, *aabb*, and *aabbb* stackings, respectively, of bcc (100) planes.

[2] M. W. Ruckman and Myron Strongin, Phys. Rev. B **35**, 487 (1987).

[3] J. W. Davenport, Phys. Rev. B **29**, 2896 (1984); R. E. Watson, J. W. Davenport, and M. Weinert (unpublished).

[4] J. W. Davenport, M. Weinert, and R. E. Watson, Phys. Rev. B **32**, 4876 (1985); **32**, 4883 (1985).

[5] R. E. Watson, J. W. Davenport, and M. Weinert, Phys. Rev. B **34**, 8421 (1986).

[6] R. E. Watson, J. W. Davenport, and M. Weinert, Phys. Rev. B **35**, 508 (1987); this paper reports results for Au alloys and lists the LASTO basis sets used here. Similar results have been obtained for Pt alloys and these will appear elsewhere.

[7] The energy is very flat on taking Pt_2Ta from the $MoPt_2$ almost to the $MoSi_2$ structure which suggests that this compound is readily distorted. This is the case: the stable phase is a "Pt_2Ta" structure which is a distorted version of $MoPt_2$ with lowered overall and individual site symmetries. Calculations of poorer quality, since the use of the muffin-tin potentials penalize crystals of low symmetry, have been done for this structure and the resulting heat of formation is represented by the cross on the figure (its position, as a function of x/y, has no meaning). The calculation was also done for a very limited number of special k points and the vertical extent of the cross is a measure of the uncertainty associated with this.

[8] P. Oelhafen, J. Phys. F **11**, L41 (1981).