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Effect of band filling on the pressure-induced structural transition in Mo-Re alloys

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We report on a detailed investigation of the combined effect of alloying and compression on the structural stability of random bcc and hcp alloys in the Mo-Re system. We use the linear-muffin-tin-orbital Green's-function method within the coherent potential approximation (LMTO-GF-CPA) and the full-potential linear-muffin-tin-orbital (FP-LMTO) method. For pure Mo we find a bcc to hcp transition pressure to take place at 620 GPa (FP-LMTO) or 730 GPa Mbar (LMTO-GF-CPA). The calculated equation of states for $Mo_{68}Re_{32}$ alloy is in good agreement with the experimental data, and the calculated bcc-hcp transition pressure is above 400 GPa. This number is much higher than the one anticipated in earlier model calculations. The agreement between the model calculations, *ab initio* calculations, and the experiment is restored when self-consistent occupation numbers of sp and d electrons are used.

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I. INTRODUCTION

Studies of structural and phase stabilities of metallic systems are of major interest both from theoretical and experimental points of view.[1–6] It has been established that in transition metals and alloys the number of d electrons per atom $\langle Z_d \rangle$ is responsible for the stability of a particular crystal structure, and that the structural sequence for the nonmagnetic $4d$ and $5d$ metals is hcp-bcc-hcp-fcc depending on the d-band filling.[1,2] The variations of Z_d with the atomic number or under high pressure may therefore lead to solid-solid structural transitions.

Experiments at extreme pressures are most valuable for the understanding of structural stabilities and phase transitions. In particular, the diamond-anvil-cell technique now allows one to attain static pressures up to several Mbar. One of the elements that attracts a lot of attention is molybdenum. Mo at ultrahigh pressures has been studied experimentally as well as theoretically.[3–5,7,8] Pure molybdenum is an interesting element for studies of structural transitions, because it has a very stable bcc structure, but still it is situated very close to the stability limit between of the bcc and hcp phases. Hixson *et al.*[8] carried out shock compression experiments and observed a discontinuity in the acoustic sound velocity data. This was interpreted as originating from a solid-solid transition occurring at a pressure of 210 GPa and a temperature of 4100 K. The transition was theoretically determined to be a bcc-hcp transition. However, in diamond-anvil-cell experiments on Mo the bcc-hcp phase transition has not been observed at pressures up to 410 GPa. Very recent experiments by Errandonea *et al.*[9] suggested that the shock transition at 210 GPa and 4100 K may be due to melting.

Moriarty[3] theoretically studied the possibility of a bcc-hcp transition in pure molybdenum, and determined that a transition can occur when 0.34 electron/atom are added to the d band of Mo. In this work a destabilization of the Mo-bcc phase was predicted to take place at an ultrahigh pressure of about 420 GPa. The theoretical results of Söderlind *et al.*[5] showed that the structural phase transition in molybdenum should take place at a pressure of 520 GPa. From the experimental phase diagram data it is estimated that increasing $\langle Z_d \rangle$ approximately by 0.5 *e*/atom destabilizes the bcc structure of group-VIB metals. The value of $\langle Z_d \rangle$ may be increased by compressing an element, but also by alloying this element with another transition metal, e.g., belonging to a neighbor group in the Periodic Table of Elements. This correspondence between compression and alloying is due to a transfer of sp electrons to the d band as a result of compression that has an effect similar to an increased band filling which is the result of alloying. Thus addition of d-electron rich metals to Mo allows one to expect that the necessary pressure to induce the bcc-hcp phase transition will decrease.

Following this idea, the transition metal alloy Mo-32 at. % Re was studied by ultrahigh pressures up to 249 GPa.[10–12] The Mo-Re alloys were chosen because the solubility of Re in solid Mo at 2500 °C is as high as 42 at. %. According to the Moriarty's calculations[3] the critical value of 0.34 *e*/atom should be sufficient for the bcc-hcp phase transition to occur even at ambient pressure. Assuming that each Re atom contributes exactly one extra d-electron to the common d band within the rigid band model, the Mo-32 at. % Re alloy has an additional 0.32 *e*/atom in the d band compared to the pure molybdenum.[11] At a pressure 193 GPa the estimated s-d charge transfer due to compression is 0.22 *e*/atom for $V/V_0 = 0.72$. Thus the total increase of the d-band filling in Mo-Re alloy (compared to pure Mo) at 193 GPa should be as high as 0.54 *e*/atom which is much higher than the theoretically expected value 0.34 *e*/atom. Still the bcc-hcp phase transition was not observed in this alloy. It appears that theory and experiment are in disagreement with each other.

Note that the situation may be quite complicated in a general case. It was shown earlier that even at ambient pressure simple rigid-band arguments may fail to predict electronic and structural properties of random alloys, particularly with increasing separation between the position of alloy components in the Periodic Table.[13–15] The high pressure adds one more degree of freedom to the problem. Thus, in order to resolve the discrepancy between theoretical and experimental results, it is necessary to perform first-principles calculations for the Mo-Re alloys that go beyond the rigid-band model. Therefore, the main aim of the present work is to investigate the pressure induced bcc-hcp phase transition in this system theoretically, and to establish its relation to the charge transfer due to alloying and compression.

II. METHOD OF CALCULATIONS

We have carried out first-principles calculations of the random bcc and hcp Mo-Re alloys over a whole interval of concentrations. In order to increase the reliability of our theoretical study we have employed two different computational methods. First, we used the linear muffin-tin orbitals Green's function method[16–23] in the tight-binding representation within the coherent potential (CPA) and atomic sphere (ASA) approximations. We have also included the so-called multipole correction to the electrostatic potential in the framework of the ASA+M technique.[22,24] The core states of Mo and Re were recalculated at each self-consistent loop. Moreover, the $4p$ states of Mo and $5p$ states of Re were treated as valence states, and the basis set included $4p$, $4d$, $5s$, and $5p$ states for Mo, and $5p$, $5d$, $6s$, and $6p$ states for Re. The calculation of the exchange-correlation potential and energy were done within the local density approximation using a Perdew-Zunger parametrization of the exchange-correlation energy functional.[25]

The atomic spheres of the alloy components were taken to be equal to the average Wigner-Seitz sphere radius in the alloy. Integration over the Brillouin zone was performed by means of the special points technique with 506 k points for bcc and 1215 k points for hcp in the irreducible part of the Brillouin zone. Energy integrals were evaluated using a semicircular contour with 50 energy points. The CPA calculations were performed for random bcc and hcp (with an ideal c/a ratio) Mo-Re alloys. The ground-state properties and equations of state were obtained from total-energy calculations for 17 different volumes at each concentration. The results were fitted by a modified Morse function.[26]

Second, we have calculated the properties of these alloys in the framework of the full-potential linear muffin-tin orbital (FP-LMTO) method.[27] In contrast to the ASA, the FP method does not use any shape approximation for the one-electron potential, and therefore it is particularly suitable for resolving small structural energy differences in ordered intermetallic compounds. The FP-LMTO technique is widely used for studies of structural phase transitions.[28] In particular, it was used for the study of the pressure-induced phase transition in pure Mo by Söderlind *et al.*[5]

Within our full-potential calculations the effect of disorder was treated by means of the so-called virtual crystal approximation (VCA), where the effect of alloying is simulated by means of an increasing (nonintegral) atomic number of the one alloy component. In our case this was the Mo atom, and therefore the basis set consisted of $4p$, $4d$, $5s$, and $5p$ orbitals. Further, we used a so-called "multiple basis" where different orbitals of l and m_l character are connected, in a continuous and differentiable way, by Hankel and Neumann functions with different kinetic energies. We used the generalized gradient approximation given by Perdew, Burke and Ernzerhof's[29] parametrization for the exchange and correlation potential. Other details of the FP-LMTO calculations are presented elsewhere.[27]

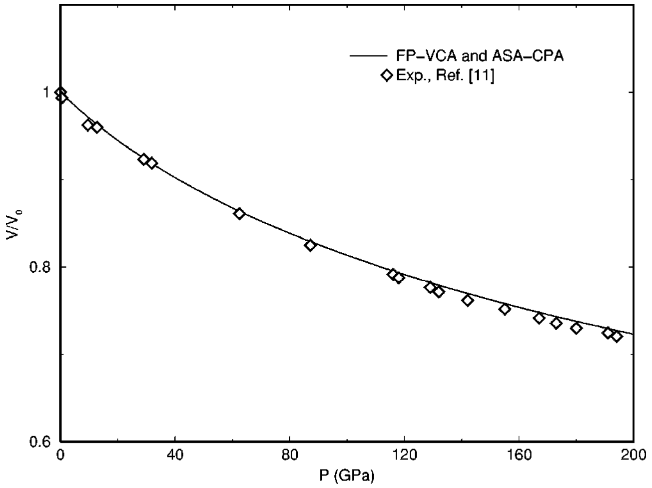

FIG. 1. Equation of states for bcc Mo-32 at. % Re alloy. Experimental data (Ref. 11) are shown by diamonds. Calculated results obtained by FP-VCA and ASA-CPA methods are undistinguishable, and are shown by the solid line.

We note that FP-LMTO calculations are superior with respect to the LMTO-ASA calculations as regards the predictions of the structural energy differences. On the other hand, the CPA employed in our ASA calculations is superior with respect to the VCA for the treatment of alloying effects. In summary, the two methods can be regarded as complementary techniques, and this combined approach has been shown to give good description of high-pressure experiments.[30] Thus we believe that the use of these methods is well justified, and allows us to address the problem of the structural stability in the Mo-Re alloys.

III. RESULTS AND DISCUSSION

In Fig. 1 we show the theoretical results obtained by the ASA-CPA and FP-VCA methods (solid line), as well as the measured equation of states of the bcc $Mo_{68}Re_{32}$ alloy sample up to 193 GPa (indicated by diamonds).[11] One can note the good agreement between the two sets of calculated data and the experimental results. We consider this agreement as an additional support for the reliability of our results.

Figure 2(a) shows a bcc-hcp transition pressure as a function of concentration of Re. One can see that for Mo-rich alloys the results obtained by FP-VCA (solid line) and ASA-CPA (dashed line) methods differ slightly, but for Re-rich alloys they are very close to each other. For pure Mo the FP method predicts the bcc-hcp transition pressure to be 620 GPa, and within the ASA it is 730 GPa. These results are higher than the results of previous theoretical investigations

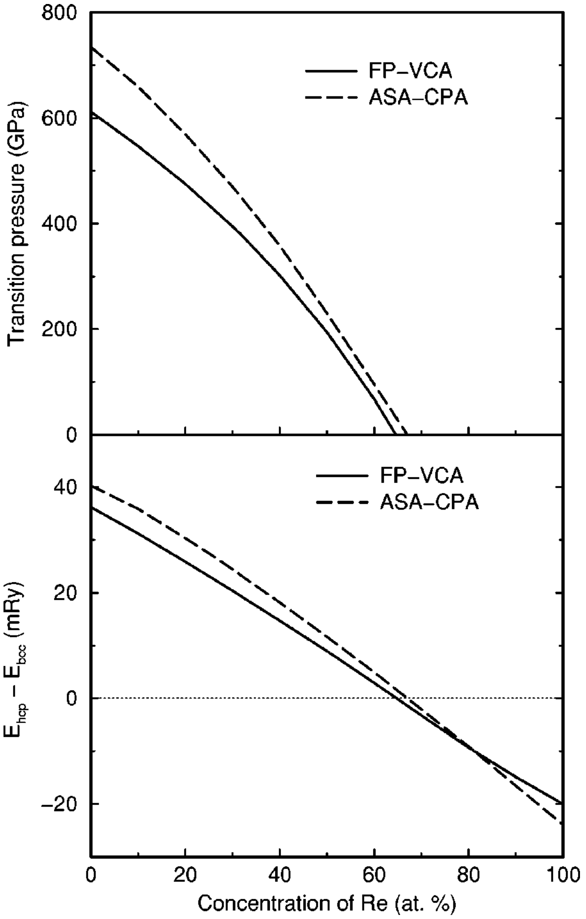

FIG. 2. (a) The transition pressure and (b) the energy difference between hcp and bcc phases as a function of concentration of Re obtained by the FP-VCA method (solid line) or ASA-CPA method (dashed line).

due to the fact that earlier FP calculations are based on local density approximation, whereas the present FP calculations are based on the generalized gradient approximation. The transition pressure for the bcc-hcp transformation for random Mo-Re alloys decreases monotonically with increasing concentration of Re. This behavior of the transition pressure is easy to explain by band-filling effects due to the additional *d* electrons which occupy the alloy *d* band as a result of alloying Mo with Re. We found that for the Mo-32 at. % Re alloy which is the highest concentration considered experimentally, a bcc-hcp transition pressure takes place at 400 GPa (FP-VCA) or 480 GPa (ASA-CPA). This is in agreement with the experimental results which show no transformation from the bcc phase for pressures up to 249 GPa.

The energy difference between the bcc and hcp phases for random Mo-Re alloys as a function of Re concentration is shown on Fig. 2(b). In our studies we found that only for alloys with concentration of Re more than 66 at. % the hcp structure becomes more energetically favourable. Note, that this number is very close in both the FP-VCA and ASA-CPA calculations. Analyzing the experimental phase diagram,[31] one concludes that the transition at ambient pressure occurs at a concentration which is well beyond the stability limit of a homogeneous solid solution.

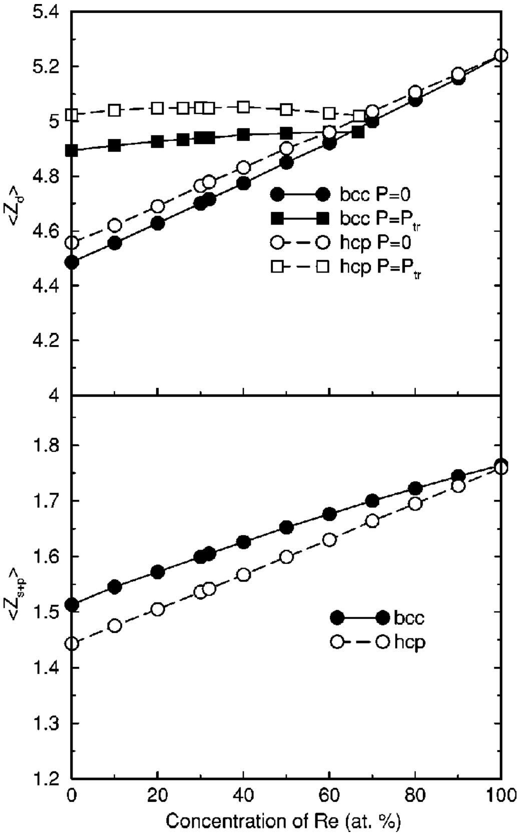

FIG. 3. (a)Average number of *d* electrons $\langle Z_d \rangle$ and (b) average number of *s* and *p* electrons $\langle Z_{s+p} \rangle$ inside the atomic sphere as a function of the Re concentration. Shown are results for bcc (solid line, filled circles) and hcp (dashed line, open circles) alloys at ambient pressure. In (a) $\langle Z_d \rangle$ at pressures corresponding to the calculated transition pressure ($P = P_{tr}$) are also shown for the bcc (solid line, filled squares) and hcp (dashed line, open squares) structures.

Thus the results of our *ab initio* calculations agree well with experiment, but disagree with the earlier model estimates. In order to understand this fact we have calculated the average number of *d* electrons $\langle Z_d \rangle$ and the average number of *s* and *p* electrons $\langle Z_{s+p} \rangle$ inside the atomic sphere as a function of Re concentration for the bcc and hcp alloys at zero pressure ($P = 0$), as well as at pressures corresponding to the calculated transition pressure ($P = P_{tr}$) over the whole concentration interval. Note that the transition pressure itself depends on the concentration, as discussed above. The results, obtained from our LMTO-ASA-CPA calculations, are shown in Fig. 3.

At this stage we would like to point out that in our calculations one expands Bloch's wave functions using a basis set of atomiclike orbitals inside the atomic sphere which can be rather artificial.[32] However, in this particular case the presented analysis is meaningful, because the lattice parameters of Mo and Re are rather close to each other, interatomic charge transfer is small, and variation of the lattice parameter is a weak function of concentration.[33] Thus though the absolute numbers $\langle Z_d \rangle$ and $\langle Z_{s+p} \rangle$ do not have a direct physical meaning, their variations as functions of concentration and pressure can be used for a physical interpretation of the phenomenon under discussion.

The most important observation one can make in Fig. 3(a) is that the *d*-band occupation $\langle Z_d \rangle$, which is sufficient to induce the transition from the bcc structure to the hcp structure in the Mo-Re alloy, shows only a small dependence on the concentration [lines denoted by squares in Fig. 3(a)]. Indeed, the variations of $\langle Z_d \rangle$ for bcc as well as hcp structures at the transition pressure with increasing concentration of Re are very small. At the same time, at ambient pressure $\langle Z_d \rangle$ for both bcc and hcp alloys increases monotonically with increasing concentration of Re. As we can see in Fig. 3(a) for pure molybdenum an addition of 0.4 *e*/atom is needed to destabilize the bcc structure. This number is close to the value of 0.34 *e*/atom reported earlier for pure Mo in Ref. 3. As expected, the difference between $\langle Z_d \rangle$ at $P=0$ and $\langle Z_d \rangle$ at $P=P_{tr}$ becomes smaller for Mo-Re alloys. Approximately at 66-at. % Re the $\langle Z_d \rangle$ at zero pressure becomes equal to the $\langle Z_d \rangle$ at the transition pressure and the hcp structure becomes more favourable energetically. Remember that $\langle Z_d \rangle$ at the transition pressure does not depend on the concentration. Thus, in order to add 0.4 *e*/atom to the alloy *d* band, one needs to supply a larger fraction of Re atoms: 0.66. This means that each new Re atom *does not* contribute exactly one *d* electron to the common *d* band due to the hybridization between sp and *d* subsystems. As one can see in Fig. 3(b), the number of *s* and *p* electrons $\langle Z_{s+p} \rangle$ also increases with increasing Re concentration. As a matter of fact, a variation of $\langle Z_{s+p} \rangle$ across the transition metal series is a known effect.[2,19] This explains the disagreement between earlier model predictions and experiment.

At the same time, one can easily correct the model by using self-consistent values of $\langle Z_d \rangle$ for the pure transition metals tabulated in the literature on the basis of first-principles calculations. For example, according to Ref. 19 the difference of $\langle Z_d \rangle$ between Mo and Re is 0.68 *e*/atom, in good agreement with our calculations. Assuming a linear dependence of $\langle Z_d \rangle$ on the Re concentration, which is also in agreement with our *ab initio* results, [Fig. 3(a)], the increase of the *d*-band filling by 0.4 *e*/atom necessary to induce the bcc-to-hcp structural transition will occur at about 60-at. % Re. This is very close to the result of the first-principles calculations where the variation of $\langle Z_d \rangle$ and $\langle Z_{s+p} \rangle$ is treated self-consistently in the complete interval of concentrations. Thus the agreement between model calculations, *ab initio* calculations, and experiments is restored.

IV. SUMMARY

First-principles calculations of random bcc and hcp Mo-Re alloys were performed over the whole concentration interval. Our calculated equations of state agrees well with experimental data. We have shown that the bcc-hcp transition pressure decreases monotonically with an increasing concentration of Re, but the rate of decrease is substantially less than that estimated in earlier model calculations. We also show that *d*-band filling at ambient conditions depends linearly on atomic concentration in this alloy, while the number of *d* electrons required for the bcc-to-hcp transition is almost independent of the concentration. We have calculated that an addition of 0.4 *e*/atom to the *d* band of pure Mo leads to a destabilization of the bcc phase at all compositions. However, at ambient pressure this requires an alloying with at least 66 at. % of Re. We show that this occurs due to a variation of the average number of *s* and *p* electrons $\langle Z_{s+p} \rangle$ as a function of concentration. We explain the disagreement between earlier model predictions and experimental data.

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