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COMMENTS

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Comment on ''Stability and the equation of state of α-manganese under ultrahigh pressure''

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Fujihisa *et al.* [Phys. Rev. B **52**, 13 257 (1995)] in their recent x-ray-diffraction experiment detected that at a pressure of about 165 GPa manganese transforms to a new phase. The crystal structure of the new phase, however, was not resolved in that work, although a bcc structure was suggested by Fujihisa *et al.* based on the small volume collapse of the α-Mn→bcc transition. In response to this unresolved phase structure of Mn, we performed first-principles total-energy calculations based on the full potential linear muffin-tin orbital method up to extreme pressures for the antiferromagnetic, ferromagnetic, and paramagnetic states in the bcc, fcc, and hcp structures. For the hcp phase we also investigated the axial stability. For very high pressures (above 165 GPa) we found that the (paramagnetic) hexagonal structure is the stable phase, in contrast to the suggested bcc phase. Our finding agrees with the general structural behavior of the paramagnetic $4d$ and $5d$ transition metals. [S0163-1829(98)05017-6]

As a group VII element manganese would be expected to crystallize in a hexagonal close-packed (hcp) structure, according to the regular structural behavior of the $4d$ and $5d$ transition series.[1–4] It is understood, however, that the crystal structures of the magnetic elements Mn, Fe, Co, and Ni do not fit into this regular structure sequence, due to their magnetic properties (see, for example, Refs. 5 and 6). While the rest of the $3d$ magnetic elements all crystallize in simple well-known structures, Mn behaves totally different. At low temperature and ambient pressure and up to considerably high pressures, Mn crystallizes in a complex structure containing 58 atoms per unit cell[7] (called α-Mn), with an antiferromagnetic (AFM) ordering of the atomic moments.[8] It is unique for an element to exist in such a complex structure (see, e.g., Ref. 7). Since this structure is likely to be the result of relatively narrow $3d$ bands in combination with magnetic ordering, one would expect it to be unstable under high pressure and that it should transform to a much simpler structure. Such a structural transformation would be a natural consequence if the complex α-Mn phase originates from its magnetic property, since the magnetic moments will decrease and finally vanish under compression. The effect of the antiferromagnetic interaction in Mn was believed to cause the atoms, occupying different crystallographic sites, to have different electronic configurations and to behave as if they were the result of atoms with different sizes.[9] Experimental efforts have been made with the purpose of identifying a phase transition under high pressure into a much simpler structure.[10,11] Very recently, at the extreme (ultrahigh) pressures of about 165–190 GPa, Fujihisa and Takemura[11] detected in their x-ray powder-diffraction experiment that Mn undergoes a structural phase transition from the α form to a simpler structure. The transition was signaled by the appearance of a Bragg peak at about 165 GPa which became stronger at about 190 GPa; this peak could be alternatively indexed[11] as the 110, 111, or 101 reflections of the bcc, fcc or hcp structures, respectively. Based on the fact that the bcc structure corresponded to the lowest volume collapse it was suggested that Mn most probably stabilizes in this structure at high pressures.[11] This is, however, in disagreement with what one would expect.[1–4] A mechanism which possibly may stabilize the bcc structure of Mn at high pressures is the hybridization between the pseudocore p band and the valence d band which becomes important at high pressure.[12] Therefore it is of interest to theoretically calculate the ground-state structure at the corresponding high compression, up to which none of the previous theoretical investigations[13–21] have been performed. In this article we present our prediction from a first-principles structural stability study using the full-potential linear muffin-tin orbital (FP-LMTO) method.[22–27] In our calculation for Mn, we treat the $3p^6 3d^5 4s^2$ electrons as valence electrons, we thus include the $3p$, $3d$, $4s$, and $4p$ components in the basis functions; and we use up to eight angular momentum components in the structure constant, $S_{lm,l'm'}$. Two E_ν sets are used to assign the p states to two different main quantum numbers. The k space is sampled with 84 and 132 k points in the irreducible wedges over the 1/48 and 1/12 Brillouin zones for the cubic and hcp structures, respectively. In the calculation for the AFM, FM, and PM states of the fcc structure, where a simple tetragonal Bravais cell with two atoms in the basis is used, the number of k points is 169 in the irreducible wedge. The antiferromagnetic structure is chosen to have alternating magnetic moment directions every second layer

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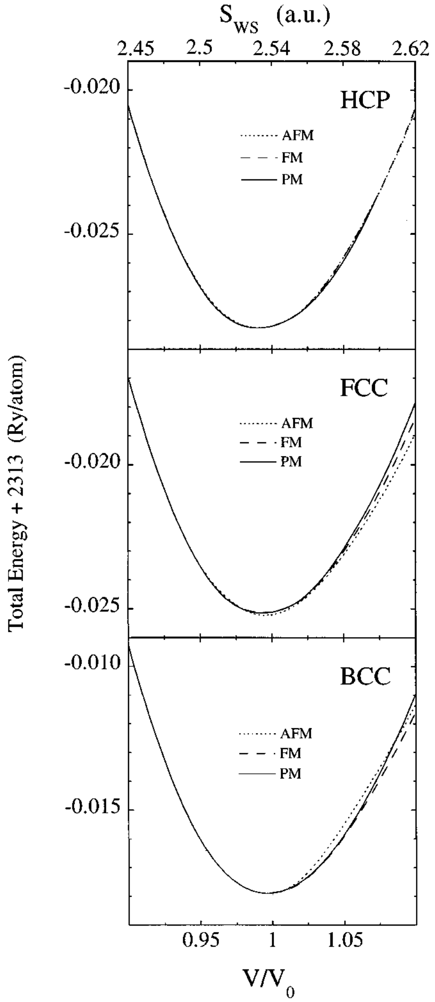

FIG. 1. Calculated total energy as a function of volume for various magnetic states for the (a) hcp, (b) fcc, and (c) bcc structures. Solid lines are used for PM, dotted lines for AFM, and dashed lines for FM. V_0 is taken to be at S_{WS}=2.54 a.u. throughout this paper.

in the [001] directions for all three structures. For all cases, the muffin-tin radii are chosen to have the same proportion to the Wigner-Seitz radius (S_{MT}/S_{WS}= 0.85).

MAGNETISM

Before advancing to the high-pressure structural stability study, we here first briefly discuss the stability of various magnetic states (AFM, FM, and PM), and derive the pressure region where the magnetic to paramagnetic phase transition occurs. All this is done for the simple structures, bcc, fcc, and hcp. From FP-LMTO calculations we obtained the total energy as a function of volume for the various magnetic states. The result is plotted in Fig. 1. S_{WS}=2.54 a.u., being approximately the theoretical equilibrium volume for the various structures at various magnetic states. The corresponding magnetic moments μ obtained for the AFM and FM magnetic structures are shown in Fig. 2; for the AFM case, the system may stabilize in an antiferro-, ferro-, ferri- or paramagnetic (PM) state. Combining the results for the total energy and the corresponding magnetic moments, the preferred magnetic states are obtained for each structure as below. (1) For hcp, the total energy for the AFM, FM, and PM states are very close to each other. For the AFM configuration, μ on each atomic site is of the order of $0.2\mu_B$ at a volume just below the equilibrium volume. As the volume expands μ increases and reaches a value of $1.2\mu_B$ at $V/V_0 \simeq 1.2$. (2) For fcc we obtain that the AFM is the preferred state in the volume region down to $V/V_0 \sim 0.95$ where the system gradually transforms to a paramagnetic state. The magnetic moment on each atom site is quite small at a volume compression of 10%, and it increases gradually with increasing volume up to $\sim 2\mu_B$ at a volume expansion of 20%. This is in the same range as the zero-temperature extrapolation of the experimental moment of δ-Mn (fcc) moment ($1.7-2.4\mu_B$) (see, e.g., Ref. 13). The PM and FM states are nearly degenerate and the magnetic moment of the FM state is correspondingly close to zero. (3) For bcc, in the vicinity of the equilibrium volume, we obtain that the paramagnetic state is favored. At about 5% volume expansion, the ferromagnetic state is favored, with the total moment reaching about $1\mu_B$ as the volume is expanded by 20%. For an antiferromagnetic starting configuration we obtained a metastable ferrimagnetic state at a volume expansion above 10%.

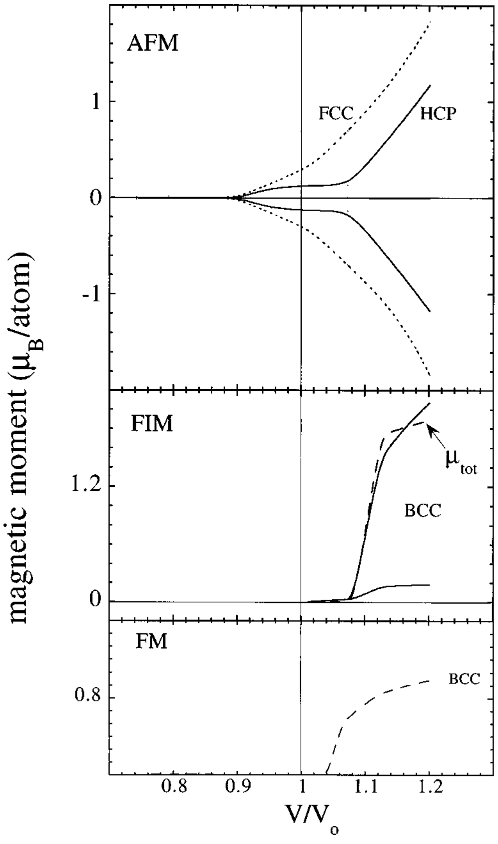

FIG. 2. Magnetic moment vs V/V_0 for the hcp, fcc, and bcc structures calculated for the antiferromagnetic (upper graph), ferrimagnetic (middle graph), and ferromagnetic (lower graph) states.

The equilibrium volume is obtained as S_{WS}=2.53 a.u. more or less independently of structure. Among the studied structures, we obtained that the paramagnetic hcp phase has the lowest energy; the energy difference between the paramagnetic hcp and fcc and bcc structures is 4 and 10 mRy,

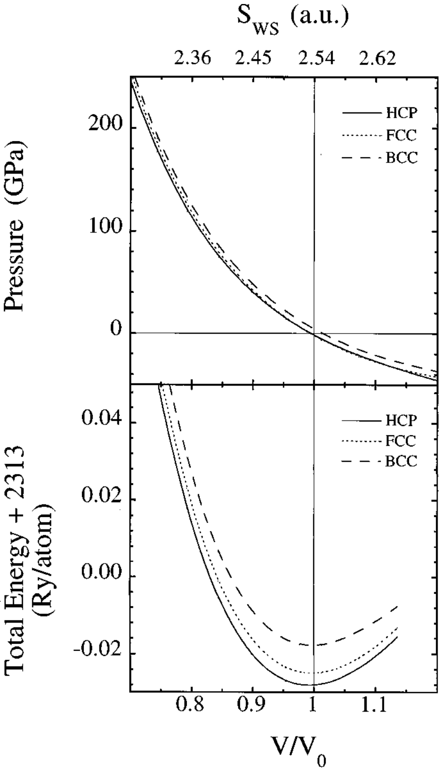

FIG. 3. Lower graph: total-energy-volume dependence of the paramagnetic state of Mn for the hcp ($c/a=1.633$) (solid line), fcc (dotted line), and bcc (dashed line) structures. Upper graph: the corresponding calculated pressure.

respectively (cf. Fig. 3). Upon compression, the magnetic moments of all structures become small at about a volume compression of 10%. (The valence band broadens under compression and results in a vanishing magnetism, which is a well understood phenomena in terms of the Stoner criterion). The corresponding pressure is ~ 40 GPa. Evidently, the simple structures transform to the paramagnetic state at much lower pressures (~ 40 GPa) than the experimental pressure (>165 GPa) region where the actual complex α-Mn begins to transform to a simple structure. We are not aware of any data for the magnetic moment of α-Mn under high compression. Sliwko, Mohn, and Schwarz[21] have performed magnetic studies for α-Mn, but only at the equilibrium volume. It would be interesting to know whether the magnetic moment decreases slower in α-Mn than in the simpler structures, yet this is beyond the scope of the present study.

TOTAL ENERGY DEPENDENCE OF VOLUME UP TO EXTREMELY HIGH PRESSURES

Regarding the structural stability the main concern of this article is in the pressure region above 165 GPa. Since this is far above the magnetic transition pressures, it is sufficient to investigate the paramagnetic state. The total energy dependence on the volume of the three structures for the paramagnetic state are plotted in the lower graph of Fig. 3, the upper graph shows the corresponding pressure. Among the simple structures the hcp structure is seen to be preferred over the entire volume range, from $V/V_0=1.2$ down to 0.7, the latter corresponding to a pressure ~ 200 GPa, as shown in the upper graph of Fig. 3. Since α-Mn is not included in this study, we can make no conclusion about the ground-state structure for Mn in the low-pressure region. But we notice that for the paramagnetic state the hcp structure is favored over the fcc and bcc structures, consistent with the structural sequence of the d transition series.[1–4] Above 165 GPa, where experimentally it is determined that α-Mn transforms to a simpler structure, the total energy yields hcp to be the ground-state structure. This is in contrast to the experimental conclusion of Ref. 11 that the new phase under extreme compression is likely to be bcc. According to the well-known structural sequence for the paramagnetic d metals, it is to be expected that at high compression, where the magnetic moment disappears, Mn should be stable in the hcp structure, since this structure is in agreement with the other members of the group VII elements.

The pressure-induced d occupation modification (here the s-d transfer) may be a source that alters the structure preference of the d transition series. However, our explicit calculation using the LMTO-atomic-sphere approximation shows that the d occupation N_d change is far too trivial to effect the structure stability in the studied pressure range (e.g., N_d changes from 5.56 to 5.62 for a volume change from $S_{WS}=2.5$ to 2.30 a.u.). In addition, if the d occupation dependence on pressure would matter at all, it should lead to a fcc structure, since the d occupancy increases under compression. We also remark that the canonical d band calculation[24] in fact marginally fails to give the hcp structure, but rather predicts the bcc phase to be the most stable structure for Mn ($N_d \simeq 5.5$). An interesting question arises here considering that the slightly larger Madelung constant of bcc (1.791 858) over that of hcp (1.791 676) would also energetically favor bcc. However, our self-consistent total-energy calculation, which correctly predicts the experimental structure sequence, is clearly in favor of the hcp structure relative to the fcc and bcc phases, the difference being of the order of 4 and 12 mRy/atom, respectively.

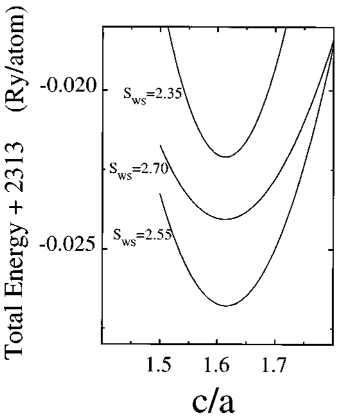

FIG. 4. The total energy as a function of the c/a ratio for three different volumes for paramagnetic hcp Mn. The energy scales have been shifted down by 0.021 and 0.042 Ry for $S_{WS}=2.70$ and 2.35 a.u., respectively, relative to the curve for $S_{WS}=2.55$. The c/a minimum is only slightly influenced when we modify the volume, e.g., for $S_{WS}=2.35$ and 2.7 a.u. we calculated the c/a ratio to be 1.614 and 1.616, respectively.

AXIAL STABILITY OF THE HCP STRUCTURE

We also performed total-energy versus c/a calculations for the hcp paramagnetic Mn. At $S_{WS}=2.55$ a.u., the preferred c/a value is obtained to be 1.617; and is found to show only a small volume dependence in the studied range (cf. Fig. 4). The total-energy difference with respect to the variation of the c/a ratio, however, is comparable to that between the bcc and fcc structures, being ~ 8 mRy over the range between $c/a=1.5$ to 1.8, as shown in Fig. 4. This suggests the importance of c/a variation for structural stability studies when hcp is concerned. In general the c/a ratio of the hcp structure varies in the range $c/a \sim 1.5$ to 1.8 across the d transition series when they are all treated as hcp metals.[28] Since the obtained $c/a=1.617$ for Mn differs only very little from the ideal c/a (1.633), we have in this study only used the ideal value when comparing with the other crystal structures.

CONCLUSIONS

Based on total-energy calculations, using the FP-LMTO method for Mn under extreme compression, we obtained that the paramagnetic hcp structure (with an optimized c/a ratio approximate to 1.63) is the ground-state structure for the pressure region 165–190 GPa. This is one of the likely structures (bcc, fcc, and hcp) observed in the x-ray-diffraction analysis of Fujihisa and Takemura.[11] In the experimental analysis the bcc phase was put forward as the most likely candidate, due to that the associated volume collapse is smallest for this structure. We have shown, however, that the calculated total energy is lowest for the hcp structure. Thus we conclude that the transition from the α structure of Mn to a more symmetric structure is not to the bcc but to the hcp phase. The preferred hcp structure is actually also consistent with the structural sequence for the paramagnetic $4d$ and $5d$ transition metals. For the hcp, fcc, and bcc structures we also studied the magnetic stability. We obtained that, for hcp, the preferred state is a PM state which, however, is almost degenerate with the AFM and FM states; and AFM for the fcc structure. For bcc, finally, we obtained PM near the equilibrium volume region and ferromagnetism above $V/V_0 \sim 1.05$. The possibility to stabilize materials in various structures by means of pseudomorphic growth might enable an experimental verification of the magnetic behavior for the symmetric structures of Mn.

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[1] C. H. Hodges, Acta Metall. **15**, 1787 (1967).

[2] D. G. Pettifor, J. Phys. C **3**, 367 (1970).

[3] A. T. Paxton, M. Methfessel, and H. M. Polatoglou, Phys. Rev. B **41**, 8127 (1990).

[4] H. L. Skriver, Phys. Rev. B **31**, 1909 (1985).

[5] D. Pettifor, *Bonding and Structure of Molecules and Solids* (Oxford Science, Clarendon, Oxford, 1995).

[6] P. Söderlind, O. Eriksson, J. M. Wills, and B. Johansson, Phys. Rev. B **50**, 5918 (1994).

[7] J. Donohue, *The Structures of the Elements* (Wiley, New York, 1974).

[8] D. Bonnenberg, K. A. Hempel, and H. P. J. Wijn, Landolt-Börnstein, New Series Group III, 19 (Springer, Berlin, 1986), p. 17.

[9] L. Brewer, Science **161**, 115 (1968).

[10] K. Takemura, O. Shimomura, K. Hase, and T. Kikegawa, J. Phys. F **18**, 197 (1988).

[11] H. Fujihisa and K. Takemura, Phys. Rev. B **52**, 13 257 (1995).

[12] See, for example, P. Söderlind, Ph.D. thesis, Uppsala University, 1994.

[13] H. Duschanek, P. Mohn, and K. Schwarz, Physica B **161**, 139 (1989).

[14] T. Asada and K. Terakura, Phys. Rev. B **47**, 15 992 (1993).

[15] M. Podgorny and J. Goniakowski, Phys. Rev. B **42**, 6683 (1990).

[16] V. L. Moruzzi, P. M. Marcus, and P. C. Pattnaik, Phys. Rev. B **37**, 8003 (1988); V. L. Moruzzi and P. M. Marcus, *ibid.* **38**, 1613 (1988); V. L. Moruzzi, P. M. Marcus, and J. Kübler, *ibid.* **39**, 6957 (1989); V. L. Moruzzi and P. M. Marcus, Solid State Commun. **71**, 203 (1989).

[17] G. Fuster, N. E. Brener, and J. Callaway, J. Fry, Y. Z. Zhao, and D. A. Papaconstantopopoulos, Phys. Rev. B **38**, 423 (1988).

[18] J. L. Fry and Y. Z. Zhao, Phys. Rev. B **36**, 868 (1987).

[19] S. Fuji, S. Ishida, and S. Asano, J. Phys. Soc. Jpn. **60**, 1193 (1991).

[20] J. Kübler, J. Magn. Magn. Mater. **20**, 107 (1980).

[21] V. Sliwko, P. Mohn, and K. Schwarz, J. Phys.: Condens. Matter **6**, 6557 (1994).

[22] J. M. Wills (unpublished).

[23] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975).

[24] H. L. Skriver, *The LMTO Method* (Springer-Verlag, Berlin, 1984).

[25] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1966).

[26] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[27] U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).

[28] B. Johansson, J. X. Zheng-Johansson, O. Eriksson, and J. M. Wills (unpublished).