# Stability and the equation of state of $\alpha$-manganese under ultrahigh pressure

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We have performed angle dispersive synchrotron-radiation x-ray powder-diffraction experiments on $\alpha$-Mn up to 190 GPa at room temperature by using a diamond-anvil cell and an imaging plate. We have obtained evidence for a structural phase transition in Mn above 165 GPa. A new diffraction peak appeared above 165 GPa, which can be most likely indexed to the 110 reflection of a body-centered-cubic structure. The volume reduction associated with the structural phase transition was estimated to be 2%. The bulk modulus and its pressure derivative of $\alpha$-Mn were determined as $B_0 = 158$ GPa and $B_0' = 4.6$, respectively. The pressure dependence of the bulk modulus indicates the decrease of the magnetic moments of Mn under pressure.

## INTRODUCTION

Manganese has four polymorphs called $\alpha$, $\beta$, $\gamma$, and $\delta$ phases. At room temperature and at ambient pressure, manganese forms the $\alpha$ phase (space group $T_d^3$-$I\bar{4}3m$), which contains 58 atoms in a cubic unit cell. This structure is analogous to the $\chi$ phase in binary or ternary intermetallic systems such as $Al_{12}Mg_{17}$ and $Fe_{36}Cr_{12}Mo_{10}$, but is unique for elemental structures. $\alpha$-Mn shows a paramagnetic to antiferromagnetic transition by lowering temperature to $T_N = 95$ K at ambient pressure. Neutron-diffraction experiments have shown that the Mn atoms in four crystallographic sites have different magnetic moments in the antiferromagnetic phase.[1] One explanation for the stability of the $\alpha$-Mn structure is that the Mn atoms with different electronic configurations behave as if they are different atoms with different sizes.[2]

Takemura *et al.*[3] have performed a structural study of $\alpha$-Mn under pressure up to 42 GPa by using the energy dispersive synchrotron-radiation (SR) x-ray-diffraction technique. They expected that the difference in Mn atoms at different sites would disappear under pressure and a structural phase transition to a simple structure would take place. However, until now, no pressure-induced phase transition has been found.

It is natural to think that such a complicated structure does not remain stable under ultrahigh pressure. The purpose of this study is to investigate the stability of the $\alpha$-Mn structure under ultrahigh pressure, and to determine the equation of state over a wide pressure range, for better understanding of the electronic and the magnetic properties of Mn under pressure.

## EXPERIMENTAL

The angle dispersive x-ray powder-diffraction experiments were performed at the Photon Factory, National Laboratory for High Energy Physics (KEK) on the beamlines 6B and 14C. The SR beams were monochromatized to the wavelength 0.6888 Å (18.00 keV) on 6B (bending magnet), and to 0.3807 Å (32.57 keV) on 14C (superconducting vertical wiggler). We used two different sample assemblies for the diamond anvil cell (DAC) for low- and high-pressure regions. The former had a pair of diamond anvils with 300 $\mu$m culet, a gasket with 80 $\mu$m $\phi$ hole and 80 $\mu$m thickness, and was utilized for a pressure range up to 80 GPa. The latter had a pair of beveled diamond anvils with 150 $\mu$m culet, a gasket with 35 $\mu$m $\phi$ hole and 33 $\mu$m thickness, and was used for higher pressures. Spring steel (PK, Hitachi Metals Ltd., Fe 98%) was used as a gasket material. A 4:1 mixture of methanol and ethanol was used as a pressure transmitting medium. The pressures were determined by the ruby fluorescence method.[4] Since the ruby fluorescence at ultrahigh pressures was very weak, the pressures above 140 GPa were estimated from the extrapolation of the equation of state of the gasket (see the next section). The accuracy in pressure was estimated to be $\pm 10$ GPa above 140 GPa.

A polycrystalline lump of $\alpha$-Mn was etched with dilute HCl solution to remove contaminants or oxides on the surface. The lump was finely ground and loaded in the DAC. The diffraction patterns recorded on imaging plates were found to be perfectly smooth. The two-dimensional image was converted to an ordinary one-dimensional diffraction pattern with the method we have already reported.[5]

## RESULTS

Figure 1 represents the diffraction patterns in the low-pressure region. The diffraction patterns are completely indexed with the $\alpha$-Mn structure. There is no significant change in relative intensity, which means that the pressure dependence of the atomic coordinates is small.

Figure 2 shows the diffraction patterns in the high-pressure region. Peaks labeled $G$ are the diffractions from the gasket, and are indexed with the hcp structure as in pure iron ($\varepsilon$-Fe). The pressures are determined in this case from the 100 and 101 reflections of the gasket. The 002 reflection of the gasket was not observed, possibly because of the strong preferred orientation in the hcp structure. We always observed the strongest peak of $\alpha$-Mn (330+411) without overlapping with the gasket lines.

A new peak indicated by an arrow appears at 165 GPa and becomes stronger at 190 GPa, the highest pressure achieved in this experiment. The peak position is $2\theta = 22.65°$ ($d = 1.754$ Å) at 190 GPa. The new peak cannot be indexed to the 002 reflection of the gasket, because the calculated peak position for the 002 reflection ($2\theta = 22.84°$, $d = 1.740$

 

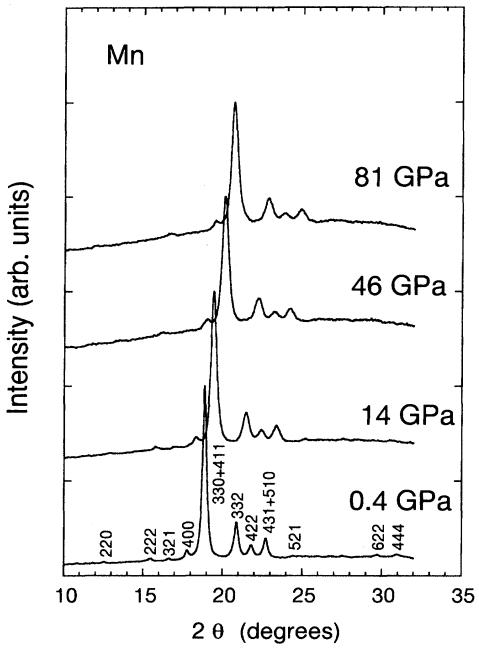


FIG. 1. X-ray powder-diffraction patterns of $\alpha$-Mn up to 81 GPa. X-ray energy was 18.00 keV.

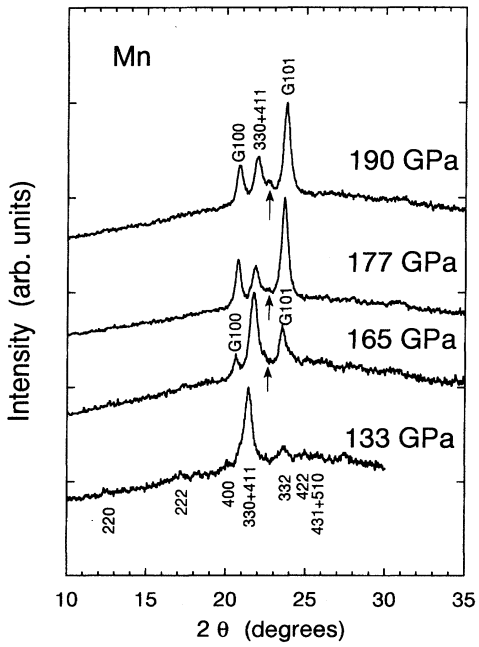


FIG. 2. X-ray powder-diffraction patterns of $\alpha$-Mn above 100 GPa. The peaks indexed $G100$ and $G101$ are the diffractions from the gasket. A peak indicated by an arrow appears above 165 GPa, which indicates a structural phase transition. X-ray energy was 18.00 keV.

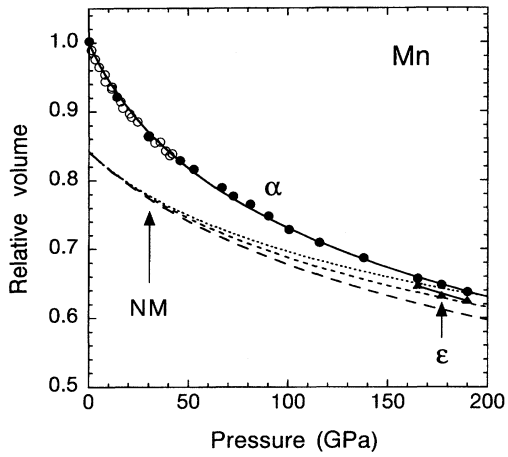


FIG. 3. The pressure dependence of the relative volume of Mn up to 190 GPa. The solid symbols are the present results and the open circles are from Ref. 3. The solid curve through the data points for $\alpha$-Mn represents a fit with the Vinet equation of state ($B_0 = 158$ GPa and $B_0' = 4.6$). The volume reduction asociated with the $\alpha$-$\varepsilon$ phase transition is about 2%. The dashed and the dotted curves represent hypothetical EOS's assumed as Mn atoms have no magnetic moments (see text).

Å) differs from the position of the new peak by more than the experimental error. We note that there is no phase transition in iron (and gasket) in this pressure range. We thus conclude that this peak comes from a new high-pressure phase of Mn. As a possible structure for the new high-pressure phase of Mn, we consider three simple metallic structures, bcc, fcc, and hcp. The new peak can be indexed to the 110 reflection of bcc, or 111 reflection of fcc, or 101 reflection of hcp. The volume reductions at the transition are then estimated to be 2.0, 9.4, and 5.6–7.4 % for bcc, fcc, and hcp,[6] respectively. Since the volume reduction does not usually exceed a few percent for structural phase transitions above 100 GPa, we choose the bcc structure as the most probable candidate for the high-pressure phase of Mn.

We name this new high-pressure phase as $\varepsilon$-Mn, which should be distinguished from the low-pressure high-temperature bcc phase $\delta$-Mn. The relative volumes of $\varepsilon$-Mn have been determined from the bcc 110 reflection by using a deconvolution program PROFIT.[7] Figure 3 shows the pressure dependence of the relative volume of Mn. The open and the closed circles represent the relative volumes of $\alpha$-Mn obtained by Takemura *et al.*[3] and in the present experiments, respectively. By fitting the two data sets for $\alpha$-Mn together with the Vinet equation of state[8] (EOS), we obtain the bulk modulus and its pressure derivative as $B_0 = 158 \pm 3$ GPa and $B_0' = 4.6 \pm 0.1$, respectively. Three triangles in Fig. 3 represent the relative volumes of $\varepsilon$-Mn.

## DISCUSSION

Moruzzi and co-workers have calculated the cohesive properties of Mn with the local-spin-density approximation by assuming the bcc (Ref. 9) and fcc (Ref. 10) structures. They also calculated the effect of pressure on the magnetic moment. In the case of the assumed bcc structure, for ex-

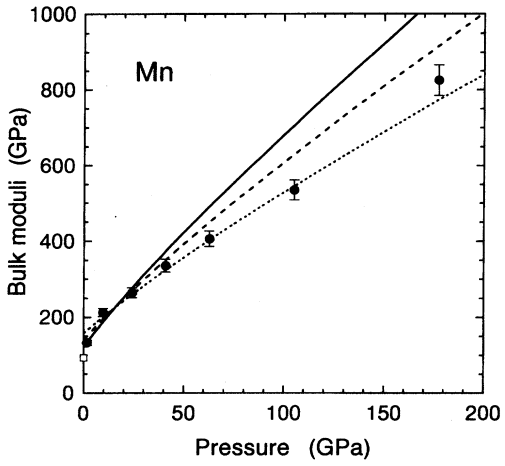


FIG. 4. The pressure dependence of the bulk modulus of $\alpha$-Mn directly obtained from the volume derivative of the observed pressure-volume curve shown in Fig. 3. The solid, dashed, and dotted curves are the bulk moduli calculated with the Vinet EOS with pairs of $B_0=121$ GPa, $B_0'=7.4$, and $B_0=140$ GPa, $B_0'=6.0$, and $B_0=158$ GPa, $B_0'=4.6$, respectively. Square represents the value at ambient pressure obtained by an ultrasonic experiment (Ref. 15).

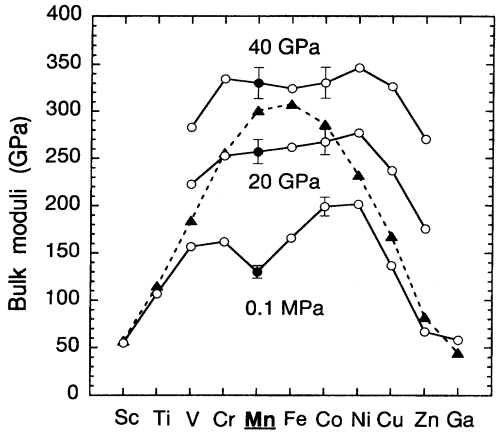


FIG. 5. Bulk moduli of $3d$ metals under pressure. The circles show the experimental values at respective pressure, and the triangles show the theoretical calculation for nonmagnetic states at ambient pressure (Ref. 10). The large discrepancies between the experimental and calculated values around Mn at ambient pressure indicate the existence of magnetic moments. The experimental values for hcp cobalt ($B_0=199$ GPa and $B_0'=3.6$) are from our recent experiments up to 79 GPa (Ref. 16). Bulk moduli of Sc, Ti, and Ga above 20 GPa are not plotted because of the phase transitions to high-pressure phases, whose $B_0$ and $B_0'$ have not been reported yet.

ample, the magnetic moment vanishes when the Wigner-Seitz radius $r_{ws}$ is reduced from 2.59 to 2.53 a.u. under pressure. This corresponds to a volume change of 6.8%, or a pressure of 13 GPa. They calculated the bulk modulus for hypothetical nonmagnetic (NM) Mn as $B_0=300$ GPa, which is considerably different from the existing experimental values (93–158 GPa). The large difference between the calculated and the experimental bulk moduli has been attributed to the existence of the magnetic moments in $\alpha$-Mn. Sliwko, Mohn, and Schwarz[11] performed the band calculation of $\alpha$-Mn based on the real $\alpha$-Mn type crystal structure. They estimated the magnetic moments for Mn atoms at different crystallographic sites, which are in reasonable agreement with the values obtained in the neutron-diffraction experiments.[1] The calculated bulk modulus of 139 GPa (Ref. 12) for the antiferromagnetic Mn is also in good agreement with the experimental values. Hence the cohesive properties (pressure-volume relationship) are proved to be a good measure of the magnetic moments. In the following, we discuss the effect of pressure on the magnetic moments on the basis of the present x-ray results.

Firstly, we estimate the EOS for hypothetical NM Mn. The volume for NM Mn at ambient pressure can be estimated to be about 84% of that of real $\alpha$-Mn, on the basis of the calculated Wigner-Seitz radius $r_{ws}=255$ a.u. by Janak and Williams.[13] Starting from this volume, we construct the NM EOS by using the Vinet EOS and the bulk modulus of $B_0=300$ GPa.[10] We assume three values (4.0, 5.0, and 6.0) for the pressure derivative of the bulk modulus $B_0'$. The corresponding NM EOS's are shown in Fig. 3 by the long-dashed, short-dashed, and dotted curves, respectively. The gap between the NM EOS's and the experimental EOS, which is the measure of the magnitude of the magnetic moments, becomes smaller with increasing pressure. This implies that the magnetic moments in $\alpha$-Mn continuously decrease under pressure, and become very small around 150 GPa. Since the EOS of the $\varepsilon$ phase is also close to the extrapolated NM EOS's, the $\varepsilon$ phase might have very small (or no) magnetic moments.

Secondly, we investigate the experimental EOS more carefully. An interesting feature is that, if we fit the $P$-$V$ data of Fig. 3 up to 20 GPa, we obtain the values $B_0=121$ GPa and $B_0'=7.4$.[14] Fitting the data up to 90 GPa, we get $B_0=140$ GPa and $B_0'=6.0$. Takemura *et al.* obtained the values $B_0=131$ GPa and $B_0'=6.6$ fitting their data up to 42 GPa.[3] Namely, depending on the increase of the pressure range to be fitted, $B_0$ systematically increases while $B_0'$ systematically decreases. Closed circles in Fig. 4 show the bulk moduli $B$ at pressure $P$, which are directly obtained from Fig. 3. For each data point in Fig. 3, we calculated the volume derivative of pressure by fitting three to five neighboring data points with a straight line. The gradient of the fitted line was taken as the bulk modulus at the averaged pressure. The solid curve in Fig. 4 represents the bulk modulus calculated from $B_0=121$ GPa and $B_0'=7.4$ with the definition

$$B(P)=-V\left(\frac{\partial P}{\partial V}(V,B_0,B_0')\right), \tag{1}$$

where $P(V,B_0,B_0')$ is given by the Vinet EOS. The dashed and dotted curves are those calculated from $B_0=140$ GPa and $B_0'=6.0$, and from $B_0=158$ GPa and $B_0'=4.6$, respectively. The value of an ultrasonic experiment at ambient pressure and temperature[15] is shown with the square ($B_0=93$ GPa). The solid and dashed curves deviate considerably from the experimental values at high pressures. On the other hand, the dotted curve cannot fit the experimental data near ambient pressure. This fact shows that the EOS of $\alpha$-Mn cannot be described well with a conventional pair of $B_0$ and $B_0'$ over

a wide pressure range. In other words, the bonding properties of $\alpha$-Mn drastically change under pressure, which prohibits the use of a simple EOS. We guess that the change is mostly caused by the decrease in the magnetic moments of Mn under pressure.

Thirdly, we compare the bulk moduli of $\alpha$-Mn under pressure with those of other $3d$ metals as shown in Fig. 5. The bulk moduli of $\alpha$-Mn at 20 and 40 GPa are taken from Fig. 4. The bulk moduli of the other elements have been calculated with Eq. (1) by using $B_0$ and $B_0'$ from literature.[17] The solid triangles show the hypothetical NM bulk moduli for each metal at ambient pressure, calculated by Moruzzi and Marcus.[10] One notices large discrepancies between the experimental and calculated values around Mn at ambient pressure (0.1 MPa), which indicate the existence of the magnetic moments. The discrepancy at Mn, however, becomes small at 20 and 40 GPa, indicating that the magnetic moments of Mn decrease under pressure.

From these three pieces of evidence, we conclude that the magnetic moments of $\alpha$-Mn continuously decrease under pressure. The disappearance of magnetism may also be related to the structural transition to the $\varepsilon$ phase. To evaluate the pressure dependence of the magnetic moments of Mn directly, we have to perform neutron-diffraction experiments under pressure. Temperature effects should also be important to clarify the relation between the crystal structure and the magnetic moments.

For the $\alpha-\varepsilon$ phase transitions in Mn, there is no theoretical calculation with which to be compared. Skriver[18] and Paxton, Methfessel, and Polatoglou[19] calculated structural energy differences for elemental metals with the local-density approximation, and found that the hcp structure is more stable than fcc and bcc structures for Mn at ambient pressure. It should be noted that the calculated energy difference between the bcc and the hcp structures gradually decreases at smaller volumes, i.e., at high pressures.[19] Magnetic effects however have not been considered in these calculations. Asada and Terakura,[20] on the other hand, calculated the total energy for bcc, fcc, and hcp Mn by taking the magnetic contributions into account. They found that the antiferromagnetic hcp phase is most stable under ambient conditions, followed by a transformation to a NM hcp phase under small compression. Hence the hcp structure seems to be the most favorable structure for hypothetical NM Mn under ambient conditions. It would be very interesting to investigate theoretically the stable structure for NM Mn under ultrahigh pressure, and to see whether the phase transition to the bcc structure is supported.

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