

Study of the Pressure-Temperature Phase Diagram of Magnesium by Synchrotron X-ray Diffraction in a Multi-anvil Apparatus

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Introduction

Magnesium (Mg) has received considerable attention as a member of alkaline-earth metal elements, the essential constituents of minerals. The particular interest in Mg is also due to the pretended simplicity of its phase diagram, which makes it an ideal candidate for theoretical studies. The room temperature (RT) equation of state (EOS) [1, 2] and the melting of Mg at high pressures [3-5] have been measured. The pressure-temperature (P-T) phase diagram has been widely investigated by using theoretical methods [6, 7]. First-principles generalized pseudopotential theory (GPT) potentials [6] predicted an hcp-to-bcc transformation at high pressure and RT. This transition has been experimentally determined at 50 GPa [2]. The high P-T phase boundary between hcp and bcc has also been calculated [7]; the boundary, according to the calculation, ends at a triple point on the melting curve near 4 GPa and 1200K, as shown in Fig. 1. If these calculations are correct, Mg is the only alkaline-earth metal that is not melting from a bcc structure at ambient pressure.

Despite the intensive theoretical study, the high P-T phase diagram of Mg has never been measured. In addition, the melting behavior of Mg near the triple point is still an open question; the melting slope does not follow the trend of other alkaline-earth metal elements and does not show any indication of the existence of a triple point [5]. The facts described above emphasize the need for a detailed experimental study of the phase diagram of Mg. Preliminary results from a study of Mg in a P-T range up to 20 GPa and 1500K are reported on here.

Methods and Materials

The combination of synchrotron x-ray diffraction and a multi-anvil apparatus gave us the possibility of experimentally studying the high P-T phase diagram of Mg. Energy-dispersive x-ray diffraction experiments were performed by using the 250-ton press installed at the GeoSoilEnviro Consortium for Advanced Radiation Sources (GSECARS) beamline 13-BM-D at the APS with a double-stage, split-cylinder T-cup assembly. Diffraction patterns were collected in an energy range of 20-130 KeV. The incident x-ray beam size was $100 \times 300 \mu\text{m}$. A Ge solid-state detector at a fixed diffraction of 5.38° was

used to detect the diffracted x-rays. Polycrystalline Mg powder of high purity (99.8%) was obtained from the Johnson Matthey Company. Temperature was determined by using a $\text{W}_{0.94}\text{Re}_{0.06}\text{-W}_{0.75}\text{Re}_{0.25}$ thermocouple. Au powder was mixed with part of the Mg sample, and its diffraction pattern was used to determine the pressure through the P-T EOS of Au [8]. NaCl was used to isolate the sample from the thermocouple, and BN was used to isolate it from the heater. The diffraction lines of NaCl, when observed, were used to double-check the pressure.

The pressure-induced transformations were monitored in three different experimental runs. The different experimental paths used for studying the P-T behavior of Mg are shown in Fig. 2. For all the P-T points, we first measured the diffraction profile of the sample and then measured the diffraction pattern of Au to determine the

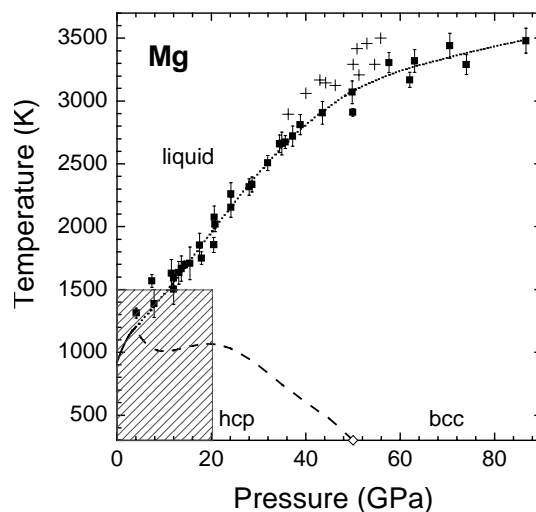


FIG. 1. High P-T phase boundary between hcp and bcc. Black squares = melting data detected by visual observation [5], plus signs = melting under shock loading [4], and diamond = RT hcp \rightarrow bcc transition [2]. Solid line = piston-cylinder differential thermal analysis (DTA) melting data [3], dashed line = calculated hcp-bcc phase boundary [7], and dotted line = simply a guide to the eye. Red area = the P-T region studied here.

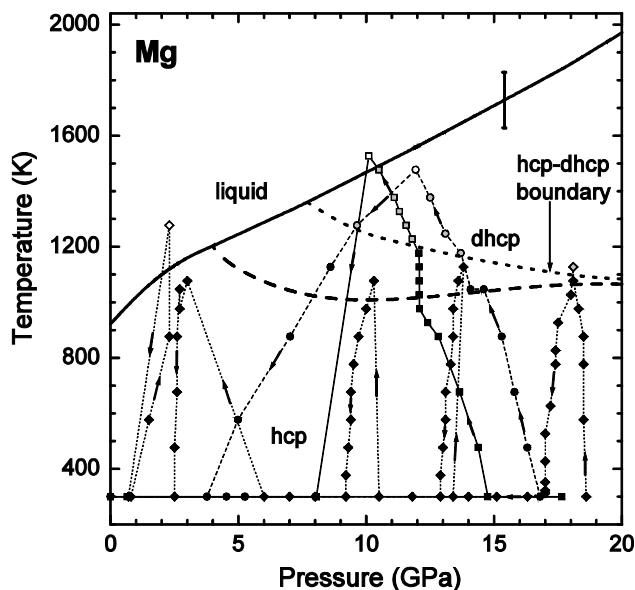


FIG. 2. Phase diagram of Mg together with experimental P - T paths. Diamonds, circles, and squares represent the three runs performed. Black symbols = the stability region of the hcp phase, gray symbols = the observance of the double hcp (dhcp) phase, and white symbols = the observance of melting. Solid lines = previous melting data [5], dashed lines = calculated hcp-bcc boundary [7], and dotted lines = first appearance of dhcp diffraction peaks.

pressure. Indexing, structure solution, and refinements were carried out by using XRDA [9] and GSAS [10] program packages.

Results and Discussion

Figure 3 shows energy-dispersive x-ray spectra recorded under different P - T conditions. The peaks arising from Au are easily identified, since their pressure shift is smaller than those of the Mg peaks. At RT, these peaks show a pressure dependence that agrees with the previously reported data [1]. At high temperature, we did not find any evidence of the existence of a bcc phase. In fact, in some cases, the samples were heated until the disappearance of the Mg peaks was observed, yet no indication of the existence of the bcc phase at high temperatures was found. The disappearance of the Mg diffraction peaks (see upper trace in Fig. 3), together with the observed increase of the background, is probably related to the onset of melting. The melting points obtained in this way agree well with previous results. It is important to note that above 1350K, the presence of a weak peak that could be attributed to the formation of a small amount of MgO is observed. The partial oxidation under high P - T conditions that was reported before in other alkaline-earth metals [11] does not affect the results

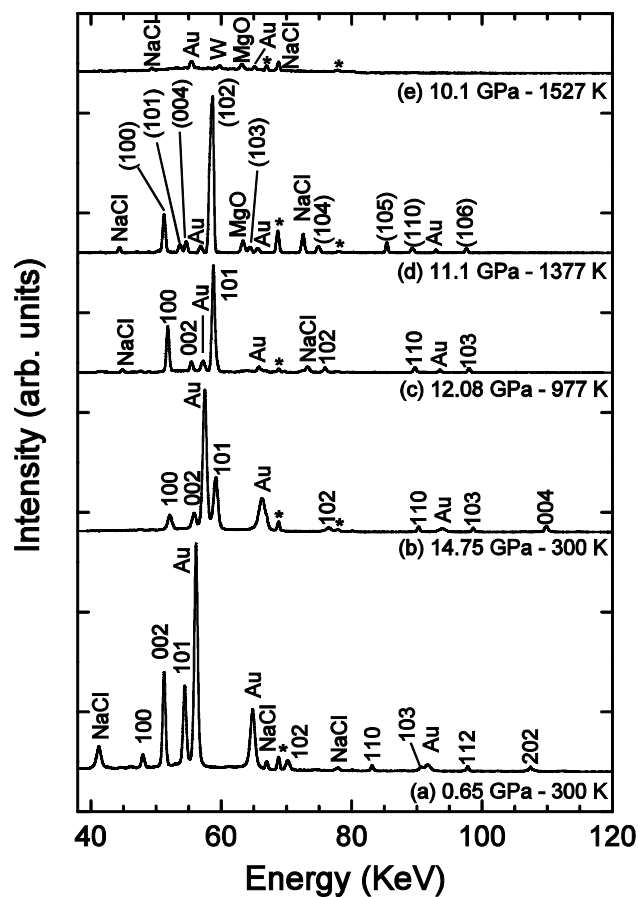


FIG. 3. Mg x-ray diffraction pattern at different P - T conditions. Miller indices corresponding to the hcp Mg structure are indicated. Au diffraction lines are shown. NaCl, W (from the thermocouple), MgO, and fluorescence (*) peaks are also labeled when observed. The upper trace illustrates the melting of Mg. The second trace shows the onset of dhcp peaks. These peaks are indexed between brackets. The background was subtracted.

on the phase diagram when the oxide peaks are well identified.

In contrast with the predicted existence of an hcp-bcc boundary line, a careful scan in temperature at different pressures reveals the splitting of the 002 peak as well as new peaks developing between the 101 and 102 peaks and the 102 and 110 peaks (see second trace in Fig. 3). The locations of these new peaks are precisely what one would expect for the 101, 103, and 105 peaks of the dhcp structure (ABACABAC.. stacking instead of ABABABAB.. stacking of the hcp structure). Incidentally, the positions of some hcp peaks (e.g., 100, 101, 102, etc.) agree with those of some dhcp peaks (e.g., 100, 102, 104, etc.). These correspondences are expected from a disorder in the atomic stacking sequence. In fact, a single stacking fault transforms the hcp structure into the

dhcp structure. The presence of the new peaks, attributed to the dhcp structure, indicates the beginning of a phase transformation, which might occur martensitically. No volume difference between the hcp and dhcp structures is observed, which is in agreement with the idea that the phase transformation occurs martensitically. In fact, since both structures differ only in their stacking sequence of planes, the transformation requires relatively small atomic displacements and thus might occur martensitically and without volume change. This kind of transformation has been observed in other close-packed metals, which has always been attributed to the developing of stacking disorders [12, 13].

In previous studies, indications of the existence of the dhcp phase at RT were found [14, 15], but in the present study, this evidence was found only at high temperatures. However, we observed that the temperature at which dhcp peaks appears decreases as the pressure increases (see dotted line in Fig. 2). Thus, the possibility that the known high-pressure crystal structure of Mg at RT is in error should be considered, particularly because in the study that reports on the observance of the bcc phase, only three diffraction lines were observed and the signal-to-background ratio was quite low [2]. Only new structural studies to pressures higher than 50 GPa could provide an answer to this question.

Regarding the melting curve of Mg, the present results might explain why the data fail to show any change in the melting slope around 4 GPa [5], as expected from the predicted hcp–bcc–liquid triple point. In fact, the occurrence of a martensitic transformation between close-packed structures (instead of a direct hcp-to-bcc transition), as reported on here, should lead to smooth behavior of the melting curve [16], like the one previously measured [5].

In summary, our preliminary results do not show any evidence of the occurrence of an hcp-to-bcc transition in the P-T range of the present study. On the contrary, they show indications of the occurrence of a martensitic hcp-to-dhcp transformation. The examination of the structural distortion (c/a ratio) as a function of P and T will probably help us better understand this transformation. This analysis and the determination of a P-T EOS are still in progress.

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References

- [1] G. L. Clendonen and H. G. Drickamer, *Phys. Rev. B* **135**, A1643 (1964).
- [2] H. Olijnyk and W. B. Holzapfel, *Phys. Rev. B* **31**, 4682 (1985).
- [3] G. C. Kennedy and R. C. Newton, *Solids under Pressure* (McGraw-Hill, New York, NY, 1963).
- [4] P. A. Urtiew and R. Grover, *J. Appl. Phys.* **48**, 1122 (1977).
- [5] D. Errandonea, R. Boehler, and M. Ross, *Phys. Rev. B* **65**, 012108 (2002).
- [6] A. K. McMahan and J. A. Moriarty, *Phys. Rev. B* **27**, 3235 (1983).
- [7] J. A. Moriarty and J. D. Althoff, *Phys. Rev. B* **51**, 5609 (1995).
- [8] O. L. Anderson, D. G. Isaac, and S. Yamamoto, *J. Appl. Phys.* **65**, 1534 (1989).
- [9] S. Desgreniers and K. Langarec, *J. Appl. Crystallogr.* **27**, 432 (1994).
- [10] A. C. Larson and R. B. Von Dreele, Los Alamos National Laboratory Report No. LAUR 86-748 (1994).
- [11] M. Winzenik and W. B. Holzapfel, *Phys. Rev. B* **55**, 101 (1997).
- [11] C. S. Yoo, P. Sonderlind, J. A. Moriarty, and A. J. Cambell, *Phys. Lett. A* **214**, 65 (1996).
- [12] C. S. Yoo, H. Cynn, P. Soderlind, and V. Iota, *Phys. Rev. Lett.* **84**, 4132 (2000).
- [13] E. A. Perez-Albuerne, R. L. Clendemen, R. W. Lynch, and H.G. Drickamer, *Phys. Rev.* **142**, 392 (1966).
- [14] H. Olijnyk, *J. Phys. Condens. Matter* **11**, 6589 (1999).
- [15] R. Boehler, M. Ross, P. Soderlind, and D. Boerker, *Phys. Rev. Lett.* **86**, 5731 (2001).