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COMMENT

Comment on ‘Study of the phase transformations and equation of state of magnesium by synchrotron x-ray diffraction’

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Abstract

In a recent paper (Errandonea *et al* 2003 *J. Phys.: Condens. Matter* **15** 1277) high-pressure, high-temperature synchrotron x-ray diffraction data of Mg were published. The authors referred to and commented on previous high-pressure studies of Mg. It is shown that some of their statements have to be corrected and more detailed explanations are necessary in order to avoid misinterpretations.

In their study of Mg, Errandonea *et al* [1] found a high-temperature dhcp lattice to be stable for pressures above 8 GPa, instead of a bcc lattice as predicted by theory [4–6]. Since the dhcp–hcp phase boundary has a negative slope, the possibility of a high-pressure dhcp phase at room temperature and its non-identification in a previous experiment [2, 7] have been discussed. The arguments for a possible non-detection of dhcp diffraction peaks in these previous experiments—a low signal-to-background ratio and possible effects of preferred orientation—can be accepted. However, the statement made in [1] ‘that in the experiment that reported a direct hcp–bcc transition at 50 ± 6 GPa and RT only three diffraction lines belonging to both the hcp and the bcc phases were observed’ is incorrect: actually five diffraction peaks were observed in this pressure range as can be noticed in the spectra at 58 and 49 GPa shown in [2]. Three of these peaks definitely are the 110, 200 and 211 diffraction peaks of the bcc phase, whereas the other two peaks are reminiscent of the hcp phase, that is 100 and 101. There is no way of indexing these five peaks to a dhcp lattice.

Furthermore, the volume at 50 GPa for the hcp phase, referenced from [2], which is given in the P – V relation of figure 5 in [1], actually is an estimate of the transition pressure and transition volume, which takes into account the quite large observed hysteresis effects and as a consequence has large uncertainties. In order to give more stringent constraints on the EOS data in the pressure range 50–60 GPa, in figure 1 the P – V data of the previous study [2, 7], which were adjusted to the pressure scale of Mao *et al* [8], are summarized together with the room temperature data of [1]. Fitting all these data to a Birch–Murnaghan equation of state gives $B_0 = 38.4$ GPa, $B'_0 = 3.7$ and $V_0 = 11.57 \text{ \AA}^3/\text{atom}$ ($=13.94 \text{ cm}^3 \text{ mol}^{-1}$), which

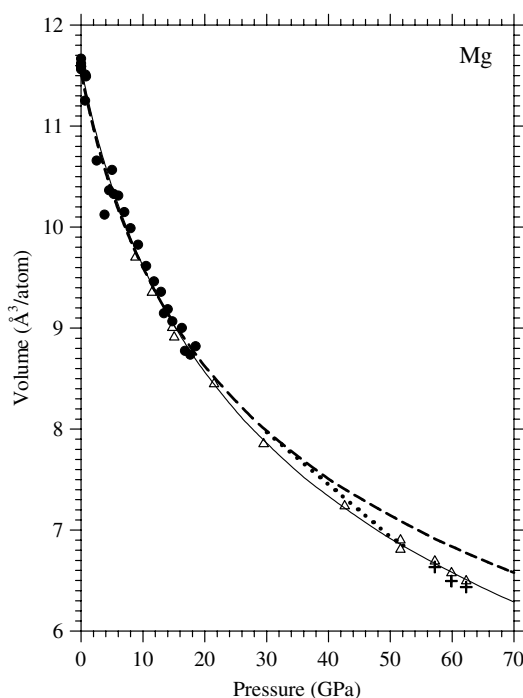


Figure 1. Compression curve of Mg at room temperature. Solid circles: hcp Mg [1], open triangles: hcp Mg [2, 7], crosses bcc Mg [2, 7]. The solid curve represents the Birch–Murnaghan fit of the hcp data from [1, 2, 7] using the fit parameters given in the text. The dashed curve is a Birch–Murnaghan fit with the parameters given in [1]. The dotted curve is the compression curve shown in figure 5 of [1].

are different from the parameters given in [1]. In particular, above 20 GPa the compression curve of [1] increasingly deviates from the experimental P – V data of [2, 7] and the Birch–Murnaghan fit using the parameters given above (see figure 1). It is also interesting to note that above approximately 30 GPa the P – V curve shown in figure 5 of [1], which was stated to ‘represent the Birch–Murnaghan fit of all measurements’, does not agree with the Birch–Murnaghan curve using the parameters given in [1] (see figure 1). The origin of the latter discrepancy remains an open question.

The authors of [1] also take the observed broadening and splitting of the E_{2g} Raman mode of hcp Mg [3] as an indication for the possible existence of a dhcp phase at room temperature in that experiment, but a detailed explanation is missing in [1] and will be given in the following. Since the hcp structure allows only the E_{2g} mode to be Raman active, the observed broadening and splitting may indeed indicate a phase transition. The dhcp structure also allows only one E_{2g} mode to be Raman active. From recent studies of some lanthanides [9] it is known that the dhcp mode has frequencies a few wave numbers below that of the hcp mode. This means that the observed anomaly (splitting) of the Raman mode in Mg above 10 GPa can indeed be reconciled with the appearance of a dhcp phase coexisting with the hcp phase up to the 50 GPa regime in that study. The disappearance of the Raman signals above 50 GPa on the other hand is another clear indication for the transition to the bcc lattice, which has no optical modes and consequently allows no Raman-active modes.

Apart from an extension of the experimental P – T structural studies and structural stability calculations including the dhcp structure also calculations of phonon frequencies for the dhcp

phase, similar to those already reported for the hcp phase [6], can be helpful in clarifying the questions on the phase diagram of Mg raised in [1]; in particular, whether the structural sequence at room temperature is hcp–bcc or hcp–dhcp–bcc.

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