Reply to Comment on 'Study of the phase transformations and equation of state of magnesium by synchrotron x-ray diffraction'

REPLY

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**Abstract**
This reply aims to clarify some of the arguments presented in a previous publication (Errandonea *et al* 2003 *J. Phys.: Condens. Matter* **15** 1277), which have been criticized in the preceding comment by Olijnyk. The article in question reported the existence of a new high-pressure and high-temperature dhcp phase in magnesium and presented strong evidence that invites one to re-study the up-to-now-established room temperature structural sequence of magnesium.

In a recent article [1] we reported that at high temperatures an hcp-to-dhcp phase transition takes place in magnesium (Mg) above 8 GPa. Based upon the observed stabilization of the dhcp phase of Mg together with previous high-pressure melting data [2] we concluded that the topology of the pressure–temperature phase diagram of Mg differs from that predicted by theory [3]. In particular, we found that up to nearly 20 GPa the dhcp–hcp phase boundary has a negative slope. On top of that, in an Mg sample quenched from melting (1530 K) at 10 GPa to room temperature (RT) at 8 GPa, the x-ray diffraction pattern measured could have been indexed only by the dhcp structure. Indications of the existence of a dhcp phase in Mg at high pressure and RT were also previously reported [4, 5]. Based upon all these facts we proposed that the correct structural sequence of Mg as a function of pressure at RT might be hcp–dhcp–bcc and not hcp–bcc as accepted until now.

We also commented in [1] that in a previous experiment performed by Olijnyk *et al* in a diamond-anvil cell (DAC) up to about 60 GPa [5], the low resolution and the low signal-to-background ratio of the measured x-ray diffraction patterns as well as possible preferred orientation effects could have conspired to hide the existence of a dhcp-to-hcp transition in Mg at RT. In his comment to our previous article [1], Olijnyk accepted our suggestions; however,
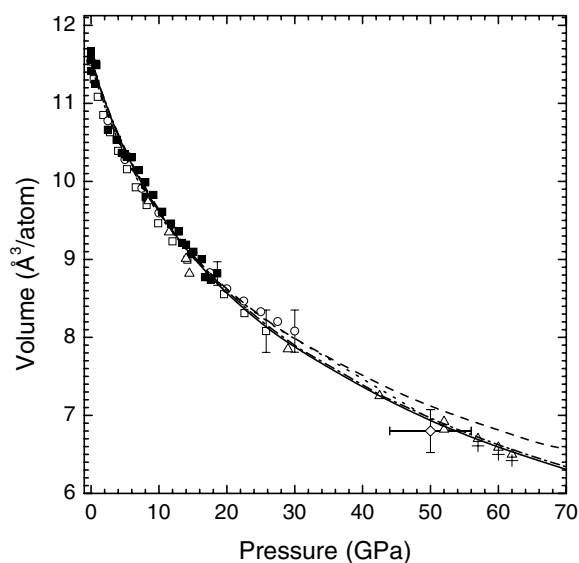
Figure 1. Compression curve of Mg at room temperature. Experimental data: (■) [1], (○) [4], (◇) [6], (□) [10], (△) [11] hcp phase, and (+) [11] bcc phase. The dashed–dotted curve represents the Birch–Murnaghan fit of all the hcp data included in the figure. The solid curve is the Birch–Murnachan fit given by Olijnyk in his comment to our article [1]. The dashed curve represents the Birch–Murnaghan fit reported in [1] and the dotted curve the compression curve mistakenly plotted in figure 5 of [1]. Typical errors for different data set are shown.

Table 1. Observed [6] and calculated d-values for Mg at 28.5 GPa. Calculations are done for an hcp structure with $a = 2.8057$ Å and $c = 4.5296$ Å and for an equivalent dhcp structure ($c = 9.1853$ Å). The calculated intensity ratios (I/I_0) for the hcp phase are also given.

d (Å)	dhcp structure hkl	hcp structure hkl	hcp structure I/I_0 (%)	Observed peaks [6]
2.469	100	100	25	Strong
2.381	101	—		Weak & broad
2.296	004	002	36	
2.174	102	101	100	Strong
1.921	103	—		Weak & broad
1.681	104	102	15	Not observed
1.474	105	—		Weak & broad
1.425	110	110	12	Medium
1.301	106	103	16	Not observed

he claimed that the statement we had made in [1], mentioning that in the measured x-ray diffraction patterns shown in [6] there are only three peaks that belong to the hcp phase of Mg (when only for d-values larger than 1.3 Å, six Bragg peaks should be observed), is incorrect. We will show in what follows that Olijnyk's claim is unfounded explaining in more detail the comments made before [1].

Table 1 shows the d-values of the Bragg peaks observed in the x-ray pattern of hcp Mg at 28.5 GPa reported in [6]. The calculated d-values for the hcp structure and the dhcp structure at the same pressure are also given. In table 1, it can be seen that in the x-ray diffraction pattern of Mg reported in figure 1(a) of [6] only three Bragg lines corresponding to hcp Mg can be clearly identified. In particular the (002), (102), and (103) reflections of hcp Mg are not

present. On top of that, the observed intensity ratio between the (100) and (110) diffraction peaks of hcp Mg substantially deviates from the expected one (measured $I/I_0 = 50\%$ instead of $I/I_0 = 25\%$). The absence of the (002), (102), and (103) hcp reflections, and the deviation of the intensities of the observed reflections from the typical ones of hcp Mg could reflect the existence of strong preferred orientation and uniaxial stress effects [7][1]. Indeed, a very similar phenomenon occurs in hcp iron, where the (002) reflection disappears under compression because of preferred orientation effects [8]. Such behaviour is common to most of the hcp metals and can be explained by an alignment of crystallites with the *c*-axis parallel to the load direction [9]. The above-described facts not only decrease the quality of powder diffraction data and increase the uncertainty in the results of the structural refinement, but also make the reliability of the structural model doubtful.

It is important to note here that the dhcp and hcp structures have the same space group ($P6_3/mmc$), but because of the different stacking order of the hexagonal planes, the dhcp unit cell is exactly double that in the hcp structure. Therefore, many correspondences are expected between the Bragg reflections of the hcp and dhcp Mg, as shown in table 1. There, it can also be seen that the diffraction peaks that distinguish the dhcp structure from the hcp structure are the (101), (103), and (105) dhcp reflections. As we commented above, in the x-ray diffraction pattern reported in [6] the peak assigned to the (101) reflection of hcp Mg has a quite lower intensity than expected and the rest of the $(10n)$ reflections were not present at all (see table 1 for details). Then, it would not be surprising that most of the $(10n)$ reflections of dhcp Mg might be absent too in the x-ray diffraction patterns reported in [6] because of the already commented drawbacks of the experiments. As a matter of fact, at the expected position for the (101)/(004), (103), and (105) reflections of dhcp Mg, three very weak and broad peaks can be observed in figure 1(a) of [6]. For all these reasons, from the data reported in [6] it cannot clearly be established whether the stable phase of Mg at 28.5 GPa is hcp or dhcp.

At higher pressures, when the bcc phase of Mg becomes stable, three new peaks attributed to the bcc phase can be observed in addition to two reminiscent peaks of the pretransition phase, which can be attributed either to hcp Mg or to dhcp Mg (figures 1(b) and (c) of [6]). We agree with Olijnyk on the fact that 'there is no way of indexing the five peaks to a dhcp lattice'. Therefore, the only conclusion that can be drawn from the data reported in [6] is that bcc Mg stabilizes at 50 ± 6 GPa (and we never challenged this conclusion in our previous work), but those data do not justify a selection of possible structural models of Mg at pressures below the stabilization pressure of bcc Mg. Summing up, as we stated in our previous work [1], from [4–6], it cannot be unambiguously determined whether the structural sequence of Mg at RT is hcp–bcc or hcp–dhcp–bcc.

Another point in Olijnyk's comment is related to the RT equation of state (EOS) we presented in [1]. He commented that the compression curve we obtained from a Birch–Murnaghan fit to the experimental data reported in [1] and in the literature [4, 6, 10] increasingly deviate above 20 GPa from Olijnyk's experimental data [11]. In figure 1 we summarize the existent pressure–volume data for Mg, including now the data reported in Olijnyk's PhD thesis (see footnote 1, [7]), which we obtained from Olijnyk's comment to our previous article and which were not available to us at the time of publication of [1]. In figure 1, it can be seen that above 10 GPa Olijnyk's data [11] always show a lower volume than that of the data we reported in figure 5 of [1]. This fact is not strange since Olijnyk *et al* [6, 11] used the ruby fluorescence technique, employing the linear pressure scale from Mao [12], to determine the pressure in his experiments, and the rest of the authors used the x-ray diffraction patterns

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[1] In a DAC, at RT a completely hydrostatic environment cannot be sustained above 13 GPa due to solidification of all known pressure media including helium. In particular, the isopropanol used as the pressure transmitting medium in [6] created highly non-hydrostatic conditions at the pressure conditions of the experiments reported in [6].

Table 2. Equation of state parameters for Mg determined in this reply compared with previously reported parameters.

B_0 (GPa)	B_0'	V_0 (Å/atom)	Reference
39.3(3)	3.6(0.7)	11.58(0.06)	This work hcp + bcc
38.9(2)	3.7(0.3)	11.58(0.06)	This work hcp
36.8(3)	4.3(0.4)	11.52(0.07)	Errandonea[a]
38.4	3.7	11.57	Olijnyk[b]
40	3.7(0.1)		Jona[c]

[a] Birch–Murnaghan fit of data reported in [1, 4, 6, 10].
[b] Birch–Murnaghan fit of data reported in [1, 6, 11].
[c] First-principle calculations [14].

from selected pressure markers [1, 4, 10]. Recently, it has been shown that the pressure scale based on ruby luminescence underestimates the pressure [13]. Therefore, it is reasonable to expect that the data obtained using this scale will show a larger compressibility, as indeed Olijnyk's data do. Because of this fact, the EOS we reported in [1] deviates from the EOS obtained by Olijnyk fitting only his [6, 11] and our data [1]. Table 2 summarizes the bulk modulus (B_0), its pressure derivative (B_0') and the atomic volume (V_0) of the EOSs. There the parameters obtained fitting all the data shown in figure 1 to the Birch–Murnaghan EOS, and the bulk modulus and its pressure derivative obtained from first-principle calculations, can also be seen. The parameters obtained considering only the hcp data and both hcp and bcc data does not differ too much from each other. As a matter of fact, the B_0 and B_0' values given in table 2 differ by less than one estimated standard deviation, which implies a good agreement between them. In fact, the relative volume difference at 70 GPa when using the different EOSs summarized in table 2 is smaller than 3%, whereas the uncertainties of the experimental data are approximately 1.5%. In order to illustrate this fact, a comparison of the different EOSs summarized in table 2 is shown in figure 1. Before closing the EOS discussion, we would like to thank Olijnyk for pointing out in his comment that the compression curve we plotted in figure 5 of [1] does not exactly agree with the compression curve obtained from the Birch–Murnaghan EOS using the parameters given by us in [1] (see table 2). The curve shown in [1] (dotted curve in figure 1) underestimates the volume above 40 GPa as shown in figure 1. This curve was mistakenly included in [1]. The correct compression curve of the EOS given in [1] is illustrated by the dashed curve shown in figure 1.

Finally, Olijnyk presented in his comment a detailed explanation for the observed broadening and splitting of the E_{2g} Raman mode of hcp Mg above 10 GPa. An explanation of this phenomenon was already offered as being due to the possible existence of a dhcp phase in Mg by Olijnyk himself [5]. We used this fact together with our and previous x-ray diffraction data [1, 4] as evidence to cast some doubts on the up to now accepted structural sequence of Mg. However, it was out of the scope of our paper to provide a detailed explanation of the pressure behaviour of the E_{2g} Raman mode of hcp Mg, since it was already explained by Olijnyk [5]. In his comment to our article [1], Olijnyk discussed more in detail the anomalies observed in the Raman mode of Mg above 10 GPa and proposed that dhcp and hcp Mg could coexist from 10 to 50 GPa. We think that the proposed coexistence could be quite plausible since a single stacking fault transforms the hcp structure into the dhcp structure [15] and pressure-induced martensitic transformations are a quite common phenomenon in the close-packed crystalline structures [16]. Extension of the experimental and theoretical studies is required to clarify this matter.

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