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The Comment of Raju et al. brings out certain interesting features of our recently developed equation of state. In an elegant way they derive simple expressions for the Anderson–Grüneisen parameter and the thermal expansivity as a function of volume. Their results are a useful extension of the theory we have presented in our previous paper. However, we wish to take the opportunity to set right a number of their deductions. In particular we would like to comment on (i) the use of the Anderson–Grüneisen parameter; (ii) the constancy of the property $zK$; and (iii) the plot of volume against $\ln(z/a_0)$. (i) The use of the Anderson–Grüneisen parameter

We agree that the property $(\partial K/\partial T)_p = 0$ is a limitation of our equation of state, provided that parameter $b$ is a constant. Unfortunately however, the Anderson–Grüneisen parameter $\delta_p$, derived from the experimental data using eqn. (10), is not a suitable property to demonstrate this limitation. The reason for this are the uncertainties in the three experimental properties, $K$, $z$, and $(\partial K/\partial T)_p$. This can be shown as follows.

The isothermal bulk modulus is derived from the adiabatic bulk modulus data of Isaak et al.\(^1\) using the relation

$$K = \frac{C_P K_S}{C_P + \frac{1}{2} K_S VT}$$

In their work Isaak et al.\(^1\) derived $K$ by making use of the thermal expansivity data of Suzuki\(^2\) which were taken to be accurate to within 5%. Using these data, Isaak et al.\(^1\) established $\delta_p$ in the temperature range 300–1800 K with an accuracy of about 6%. More accurate volume–temperature data became available through the measurements of Dubrovinsky and Saxena\(^3\) and Fiquet et al.\(^4\) in the temperature range 300–3100 K. The volume measurements of these two groups are consistent with each other to within 0.1%. Although Dubrovinsky and Saxena\(^3\) and Fiquet et al.\(^4\) derive expressions for the thermal expansivity with an accuracy of 2%, calculated thermal expansivities may differ by as much as 4–5% at temperatures below 800 K. At temperatures larger than 1000 K, the deviations are less than 2%. The upshot of this is that a 2% experimental error in thermal expansivity combined with a 1% error in heat capacity, results in an error in the isothermal bulk modulus comparable with that in the adiabatic bulk modulus.

The last source of uncertainty in $\delta_p$ is the error introduced by $(\partial K/\partial T)_p$. The isothermal bulk modulus data have to be smoothed to derive values for this property. Inspecting the isothermal bulk modulus data reveals their non-linearity in temperature. In Fig. 1 we have plotted the Anderson–Grüneisen parameter using different expressions for $(\partial K/\partial T)_p$. In a first step we took the derivative independent of temperature resulting in a description of the isothermal bulk modulus data outside the experimental uncertainty for temperatures smaller than 450 K. This discrepancy is not

![Fig. 1 Plot of the Anderson–Grüneisen parameter vs. temperature at 1 bar pressure for MgO. $\delta_p(\partial K/\partial T)_p$ has been obtained by smoothing the isothermal bulk modulus ($K$) data with a linear function of temperature. $\Delta \rho(\partial K/\partial T)_p$ has been obtained by smoothing the isothermal compressibility ($\rho$) data with a quadratic function of temperature. The error bars have been calculated with experimental uncertainties of 1% in $C_p$, 0.1% in $V$, and 2% in $z$. Experimental errors in $K_S$ have been taken from Isaak et al.\(^1\) The solid curve has been derived with our equation of state for MgO.](Image 343x158 to 508x310)
removed by taking the isothermal compressibility as a linear function of temperature. The calculated Anderson–Grüneisen parameter is therefore not reliable at low temperatures. In a next step we used a quadratic function for the isothermal compressibility (κ). We prefer to take this property rather than the isothermal bulk modulus for reasons that a quadratic expression for κ(T) does not result in negative values for K at any temperature. We conclude from Fig. 1 that δ T is quite sensitive to the model description of (δK/δT) P and that it cannot be used to decide if (δK/δT) P = 0 is a limitation in the formalism for MgO.

(ii) The constancy of the property azK

One way to avoid the problem mentioned above, is to divide δ T by (δK/δT) P and plot the property azK (which in our formalism should be constant, according to Raju et al.) against temperature, see Fig. 2. This figure not only shows that the experimental data are well described within experimental uncertainties, but also that azK does not become really constant for temperatures higher than about 900 K. Besides, eqn. (21) is generally valid and does not require that azK is constant.

On the other hand it does follow from our equation of state that azK is independent of pressure at constant temperature, and thus (azK/∂P) P = 0. Starting from

\[
\frac{\partial (azK)}{\partial P} = K \frac{\partial a}{\partial P} + a \frac{\partial K}{\partial P}
\]

and the generally valid eqn. (17) in the Comment, it follows that

\[
\frac{\partial (azK)}{\partial P} = \frac{1}{K} \frac{\partial K}{\partial T} + a \frac{\partial K}{\partial P}
\]

Following Raju et al., our equation of state results in (azK/∂P) P = δ T, leading to the pressure independence of azK.

(iii) The plot of volume against ln(az/z0)

Finally we note that a plot of volume vs. ln(az/z0) does not result in a straight line when our equation of state is used. As presented in our paper, the a(T) function has been derived using volume data from various sources. This function is used as input in our equation of state and linearity would be coincidental. The discrepancy between Raju et al.’s and our deduction stems from the integration of eqn. (19). Despite the validity of the differential at constant temperature, it not automatically follows that the integration may be performed at constant pressure in the temperature direction. This would require that (az/∂V) T = (az/∂V) pr(T) = 0 and (az/∂V) pr(T) = (az/∂T) pr(T) = (1/azV)(az/∂T) pr(T) = (−1/TV)). Using our equation of state, the two differentials take different forms. Whereas eqn. (20) in the Comment, representing the integration of eqn. (19) in the pressure direction is valid, the same is not true for the integration in the temperature direction, i.e.

\[
a(T) = a(T) e^{b(−V_T−V_0/β)}
\]

is not valid. As a result, a plot of volume vs. ln(az/z0) is not expected to be a straight line; that this statement is true clearly follows from Raju et al.’s Fig. 2 where the calculated plot of V vs. ln(az/z0) is in full agreement with the ‘experimental data’.

References