Reply to "Comment on 'Reappraisal of experimental values of third-order elastic constants of some cubic semiconductors and metals' "

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In his Comment [Phys. Rev. B **74**, 146101 (2006)], Mañosa claims that other methods of calculation can obtain reliable values of third-order elastic constants from data for acoustic measurement under uniaxial stress, from data sets which fail under multivariate linear regression analysis (MVLA). His analysis does not consider errors. We show that his method leaves errors on the derived values, orders of magnitude larger than those obtained by MVLA, and that his values are therefore completely unreliable.

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The determination of third-order elastic constants from acoustic data, stress coefficients of acoustic velocities, uses n simultaneous linear equations to relate n data to m elastic constants, with $n \geqslant m$. Mañosa claims that alternative methods of calculation can obtain reliable values from data sets that fail under multivariate linear regression analysis (MVLA).[1] This claim challenges the Gauss-Markov theorem according to which the MVLA makes the best use of the information in the data set. Moreover, the methods used by Mañosa do not provide the analysis of errors that is intrinsic to MVLA, and his resulting values lack reliability.

The n simultaneous equations for cubic crystals (with $m=6$) are given in full ($n=14$) in Eq. (7) in our paper[3] and the reduced set ($n=9$) for uniaxial stress data alone are given as Eq. (2) in Mañosa.[1] They are of the form

$$\bar{y} = \mathbf{X}\beta, \tag{1}$$

where the symbols are defined in Refs. 1 and 3. Mañosa[1] notes that we copied the mistake in the original expressions given by Thurston and Brugger.[4] This mistake, $(b-a)$ for $2b$ in line 8 of our Eq. (7), was corrected by McSkimin and Andreatch,[5] and by Thurston and Brugger in their erratum.[6] We used the corrected term in all of our calculations.

The data under discussion comes from Gonzales-Comas and Mañosa.[2] From their paper, we took the stress differentials of fractional changes in acoustic velocities. Using the density $\rho_0=7.090\ \mathrm{g\,cm^{-3}}$, and second-order coefficients $c_{11}=139.7$ GPa, $c_{12}=124.9$ GPa, and $c_{44}=97.7$ GPa (also from their paper), we calculated the stress coefficients of the acoustic stiffnesses which, in the order required for the vector representation of Eq. (1) are

$$(\rho_0 W_i^2)' = (-3.22, -6.96, -4.88, -7.26, -3.52, -2.54, -1.38, +3.27, 1.95) \tag{2}$$

(in dimensionless units). Adding the other terms required yields

$$\bar{y} = (-13.2, -7.28, +4.06, -13.3, -0.655, -0.678, +3.00, +3.49, -2.68). \tag{3}$$

Carrying through the experimental errors given by Gonzales-Comas and Mañosa[2] gives the errors on these values as

$$\varepsilon_y = (\pm 0.5, \pm 1.2, \pm 0.8, \pm 0.3, \pm 0.6, \pm 0.4, \pm 0.9, \pm 0.7, \pm 0.4). \tag{4}$$

Mañosa[1] recommends the method used by Verlinden *et al.*,[7] in which three lines of Eq. (1) are used to obtain c_{111}, c_{112}, and c_{123} from three data alone. These values are then carried forward into the subsequent calculation of c_{144}, c_{166}, and c_{456}. One of his reasons for doing this is that these three data happen to have large stress coefficients and hence, he says, small fractional errors. This is a misconception. The errors arise predominantly from the uncertainty in uniaxial strain (this is why hydrostatic data are more accurate), not from the acoustic velocity measurements. All data are then expected to have the same fractional error, and so the absolute errors, which are what matter in this calculation, should be largest for the largest stress coefficients. MVLA treats all errors as random numbers drawn from the same distribution. If it were worth the refinement, the data and the corresponding entries in the matrix **X** could be rescaled to make it so; this would have the effect of increasing the weight of the more accurate data. Mañosa's method increases the weight of some of the less accurate data (y_2 and y_8).

With rounded numerical values in the reduced 3×3 **X** matrix, the three lines are

$$\begin{pmatrix} y_2 \\ y_4 \\ y_8 \end{pmatrix} = \begin{pmatrix} 0.0108 & -0.0337 & 0.0229 \\ 0.0216 & -0.0242 & 0 \\ -0.00604 & 0.01685 & -0.0108 \end{pmatrix} \begin{pmatrix} c_{111} \\ c_{112} \\ c_{123} \end{pmatrix}, \tag{5}$$

where the elements of **X** are in units of GPa^{-1}. Mañosa[1] claims that this solves to $c_{111}=-1790$ GPa, $c_{112}=-1050$ GPa, and $c_{123}=-980$ GPa. He gives no error estimates; indeed none are generated since Eq. (5) is not overdetermined. Mañosa's Table I (particularly the scatter between the values of columns B and C) implies errors of the order of ±20 GPa, while Gonzales-Comas and Mañosa gave errors of ±100 to ±150 GPa. We may calculate the $\bar{y}$ values corresponding to Mañosa's c_{IJK}, obtaining $(y_2, y_4, y_8)=(-6.392, -13.293, 3.716)$. These are similar to but not identical with the values we used of $(-7.28, -13.3, 3.49)$. This discrepancy would be worth dealing with if reliable c_{IJK} could be obtained from these data. However, they cannot. To see this, we invert Eq. (5) to form

$$\beta = \mathbf{X}^{-1}\bar{y}, \tag{6}$$

and with numerical values for $\mathbf{X}^{-1}$ in GPa, this is

$$\begin{pmatrix} c_{111} \\ c_{112} \\ c_{123} \end{pmatrix} = \begin{pmatrix} -4703 & -389 & -9965 \\ -4203 & -389 & -8907 \\ -3924 & -389 & -8407 \end{pmatrix} \begin{pmatrix} y_2 \\ y_4 \\ y_8 \end{pmatrix}. \tag{7}$$

The large numbers, up to nearly 10 000 GPa, in the matrix mean that errors of ±100 GPa in the elastic constants require errors better than ±0.01 in the y values and hence in the pressure coefficients. This is wholly implausible. Even for silicon, which is a far easier material to measure accurately, the scatter in the uniaxial pressure coefficients between different authors[5,8] is about ±0.01 (see Table II of Ref. 3). The errors ε_y in the y values calculated from the experimental errors given by Gonzales-Comas and Mañosa[2] are, as given in Eq. (4), around 0.5, so the errors in the c_{IJK} using Eq. (7) cannot be less than a few thousand GPa. Using the $(y_2, y_4, y_8) = (-7.28, -13.3, 3.49)$ that we found, does indeed yield values for c_{111}, c_{112}, and c_{123} all of the order of −4000 GPa. This very high sensitivity to error in the data occurs because the matrix $\mathbf{X}$ of Eq. (5) is very nearly singular, with a determinant of 5×10^{-8}. Even the small changes in $\mathbf{X}$ obtained by rounding to the nearest 0.0001 in Eq. (5) cause large changes of the order of a factor of 2 in the elements of $\mathbf{X}^{-1}$ in Eq. (7).

The values for c_{111}, c_{112}, and c_{123} in Mañosa's Table I, column B are thus unreliable and implausibly precise. It follows that the values calculated using them for c_{144}, c_{166}, and c_{456} are equally defective. In his Table I, column C, Mañosa gives the results of another calculation using an iterative least-squares method under constraints ($c_{IJK} < 0$, etc), but with insufficient detail for us to analyze its results and its handling of errors. Nor is any more detail of the calculation given in the original papers.[2,9,10] In principle such methods ought to be equivalent to MVLA. Since the results are so similar to the results obtained from the Eq. (5) method, it is clear that the actual implementation replicated the defects of the Eq. (5) method and lacked the essential analysis of errors that this work requires.

A nice illustration of the theoretical advantage of MVLA is that the first line of the inverse of the $(n=9)$ version of Eq. (1) is

$$c_{111} = (-118, 4, -242, 16, -248, -124, -287, -27, -124)\bar{y}. \tag{8}$$

These numerical values (in GPa) are far smaller than those of the first line of Eq. (7), so that the errors in $\bar{y}$ feed through to yield much smaller errors in c_{111}. And to illustrate again the advantages of using hydrostatic data too, the first line of the full $(n=14)$ matrix for hydrostatic as well as uniaxial data is

$$c_{111} = (-67, 9, -5.5, 9, -3, -6, 6, 15, 23, -5, -2, -38, -5, -2)\bar{y}, \tag{9}$$

where the first five elements are for the hydrostatic data and the last nine for the uniaxial. This shows that including the hydrostatic data reduces the sensitivity to uniaxial errors by another order of magnitude.

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