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

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In a recent paper A. S. Johal and D. J. Dunstan [Phys. Rev. B **73**, 024106 (2006)] have applied multivariate linear regression analysis to the published data of the change in ultrasonic velocity with applied stress. The aim is to obtain the best estimates for the third-order elastic constants in cubic materials. From such an analysis they conclude that uniaxial stress data on metals turns out to be nearly useless by itself. The purpose of this comment is to point out that by a proper analysis of uniaxial stress data it is possible to obtain reliable values of third-order elastic constants in cubic metals and alloys. Cu-based shape memory alloys are used as an illustrative example.

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In a recent paper Johal and Dunstan[1] have analyzed a large amount of published data on the hydrostatic and uniaxial pressure dependence of the ultrasonic wave velocity in cubic semiconductors, elemental metals, and some miscellaneous materials. These authors conclude that uniaxial data sets are not adequate to yield third-order elastic constants (TOEC), C_{IJK}, in the absence of hydrostatic data. Here I show that a proper analysis of the uniaxial experimental data yields reliable values for the complete set of TOEC in cubic alloys.

Johal and Dunstan have used multivariate linear regression analysis (MVLA) to obtain C_{IJK} from the raw data. For semiconductors, MVLA provides C_{IJK} values, which are in good agreement with published data. For metals, the MVLA applied only to uniaxial stress data provide C_{IJK}, which bear no resemblance to the published values. Including hydrostatic pressure data, when available, substantially improves the results.

In their analysis, the independent C_{IJK} form a six-dimensional vector β, which is obtained from the experimental data by

$$\beta = \frac{\mathbf{X}}{\mathbf{X}^{\mathrm{T}}\mathbf{X}}\bar{y}, \tag{1}$$

where $\bar{y}$ is a 14-dimensional vector containing the pressure derivatives of the ultrasonic velocities and combinations of SOEC, and $\mathbf{X}$ is a 14×6 matrix obtained from the Thurston and Brugger relationships.[2] The first five lines in Eq. (1) relate the hydrostatic pressure derivatives to C_{IJK} and the remaining nine lines relate the uniaxial pressure derivatives. The authors have analyzed experimental data by using either the full matrix $\mathbf{X}$ (referred to as 14 in their tables) when hydrostatic data are available or the submatrix with only the nine uniaxial data (referred to as nine). By arguing that hydrostatic data are affected by a lower error, the authors split the $\mathbf{X}$ matrix into a 5×3 matrix relating hydrostatic data to the linear combinations $d_1=C_{111}+2C_{112}$, $d_2=C_{123}+2C_{112}$, and $d_3=C_{144}+2C_{166}$ and a 9×3 matrix with uniaxial data in which the previously obtained d_1, d_2, and d_3 from hydrostatic data are included. They conclude that it is best to handle hydrostatic data and uniaxial data separately.

For the sake of clarity, the equations relating the uniaxial data to the full set of C_{IJK} are expressed below.

$$(\rho_0 W_i^2)' + \begin{pmatrix} -a(C_{11}+C_{12}+2C_{44}) \\ -a(C_{11}-C_{12}) \\ 2bC_{44} \\ -2aC_{11} \\ -(a-b-2c)C_{44} \\ -(a-b+2c)C_{44} \\ -\frac{1}{2}(C_{11}+C_{12}+2C_{44})(a-b+2c) \\ -\frac{1}{2}(C_{11}-C_{12})(a-b-2c) \\ -2aC_{44} \end{pmatrix} = \begin{pmatrix} a/2 & \frac{1}{2}(3a-b) & -b/2 & -b & 2a & 0 \\ a/2 & -\frac{1}{2}(a+b) & b/2 & 0 & 0 & 0 \\ 0 & 0 & 0 & a & (a-b) & 0 \\ a & (a-b) & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2}(a-b) & \frac{1}{2}(3a-b) & -2c \\ 0 & 0 & 0 & \frac{1}{2}(a-b) & \frac{1}{2}(3a-b) & 2c \\ \frac{1}{4}(a-b) & \frac{1}{4}(5a-3b) & \frac{1}{2}a & a & (a-b+4c) & 0 \\ \frac{1}{4}(a-b) & \frac{1}{4}(a+b) & -\frac{1}{2}a & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2}(a-b) & \frac{1}{2}(3a-b) & 2c \end{pmatrix} \begin{pmatrix} C_{111} \\ C_{112} \\ C_{123} \\ C_{144} \\ C_{166} \\ C_{456} \end{pmatrix}, \tag{2}$$

where $a=-s_{12}$, $b=s_{11}$, and $c=\frac{1}{4}s_{44}$ are the elastic compliances.

Note that there is a mistake in line 8 of Eq. (7) given by Johal and Dunstan.[1] They use the original expressions given by Thurston and Brugger in their first paper,[2] but later those authors published an erratum[3] with corrected expressions. These corrected expressions are those given here in Eq. (2). The 9×6 matrix on the right-hand side will be referred to as **A** from now on. Then, Eq. (2) is expressed as

$$\bar{y}=\mathbf{A}\beta. \tag{3}$$

The application of MVLA to the nine uniaxial data in metals and alloys yielded meaningless C_{IJK} values in many cases and therefore the authors concluded that uniaxial data on metals turns out to be nearly useless. Using their MVLA all nine equations are treated equally. Since the set of equations in Eq. (2) is overdetermined and the experimental parameters are affected by errors, there are many possible combinations of C_{IJK} that may satisfy Eq. (2). A crude application of MVLA without further analysis of the physics of the investigated materials can easily yield meaningless C_{IJK} as those obtained by Johal and Dunstan for Cu and Cu-Al-Ni. There are, however, some procedures to circumvent these inconveniences, which can yield the correct set of C_{IJK}.

A detailed analysis of the equations in Eq. (2) shows that Eqs. (2), (4), and (8) form a closed set, which enables C_{111}, C_{112}, and C_{123} to be directly obtained. Equations (3), (5), (6), and (9) only contain C_{144}, C_{166}, and C_{456}. Moreover, for cubic materials the ultrasonic velocities included in Eqs. (2), (4), and (8) exhibit the strongest stress dependence (particularly the slow shear modes 2 and 8) and therefore the associated fractional error in the measurements is much less than for the other modes. Hence, a good way to obtain the complete set of C_{IJK} is to first solve the system of Eqs. (2), (4), and (8), which yield to reliable values for three TOEC. These values are then input into the remaining equations. The remaining set of equations can be solved by several methods. This method was used by Verlinden *et al.*[4] to obtain the TOEC of Cu-Zn-Al, and later by Gonzàlez-Comas *et al.*[5] for Cu-Al-Ni. In the procedure of solving the equations it is convenient to impose physical constraints, which eliminate meaningless solutions for C_{IJK}. A set of constraints, which can be used for cubic systems is[6] $C_{IJK}<0$, $C_{111}<C_{112}$, and $C_{112}<C_{113}$.

An independent method was used by Gonzàlez-Comas *et al.*[7–9] to obtain the TOEC of Cu-Al-Ni and Cu-Al-Be. It is based on a least-mean-square method, which seeks C_{IJK} values that minimize the error ε defined as

$$\varepsilon=\sum_{j=1}^{9}\sqrt{[(\mathbf{A}\beta)_j-\bar{y}_j]^2}. \tag{4}$$

The desired solutions are numerically obtained by an iterative procedure under the constraints previously mentioned. By using the raw data for Cu-Zn-Al given by Verlinden *et al.*,[4] the maximum discrepancy in the C_{IJK} values obtained by this method with those reported by these authors was less than 2%.[8] A refinement of the obtained values can be achieved by allowing modifications of the experimental values within a range covered by each experimental error bar. The robustness of the method was further confirmed by including the hydrostatic values previously measured for Cu-Al-Be (Ref. 10), which yielded values consistent with those obtained with uniaxial data solely. In Table I, I list the values determined by using the previously mentioned methods (from Johal *et al.*,[1] column *A*, from Verlinden *et al.*,[4] column *B*, and from Gonzàlez-Comas *et al.*,[8] column *C*) for the Cu-Al-Ni system.

TABLE I. Third-order elastic constants of Cu-Al-Ni, derived from the methods used by Johal *et al.* (Ref. 1), column *A*, Verlinden *et al.* (Ref. 4), column *B*, and Gonzàlez-Comas *et al.* (Ref. 8), column *C*.

TOEC	*A*	*B*	*C*
C_{111} (TPa)	−0.089	−1.79	−1.79
C_{112} (TPa)	0.476	−1.05	−1.01
C_{123} (TPa)	0.438	−0.98	−0.96
C_{144} (TPa)	−0.132	−0.93	−1.00
C_{166} (TPa)	−0.292	−1.08	−1.08
C_{456} (TPa)	−0.072	−0.60	−0.61

Finally, it is worth remarking that the reliability of the C_{IJK} data reported for several Cu-based shape memory alloys enabled a general behavior for the anharmonicity of this family of alloys to be established.[11] This behavior was fully consistent with that found for the Grüneisen parameter associated with the shear modes, obtained from hydrostatic pressure data.

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