PHYSICAL REVIEW B VOLUME 22, NUMBER 12 15 DECEMBER 1980

# Isotropic-continuum-model calculation of the thermal expansion of alloys from third-order elastic constants: Application to CuAl

H. M. Gilder
*Laboratoire Léon Brillouin, 91190 Gif-sur-Yvette, France*

J. P. Ganne
*Section d'Etudes des Solides Irradiés, Centre d'Etudes Nucléaires, 92260 Fontenay-aux-Roses, France*

(Received 15 April 1980)

A simplified model calculation of the thermal expansion of alloys from their third-order elastic constants within the context of a Debye, isotropic continuum is presented. The model is applied to the CuAl system. The averaging techniques used to convert the cubic alloy to its isotropic equivalent all yield the same value of the impurity-concentration normalized fractional change in thermal expansion $d\beta/\beta dC_i$, within the large uncertainty imposed by the error bars in the experimental, input data. The most likely value of $d\beta/\beta dC_i$ that emerges from the present calculation is $-(5\pm3)\times10^{-3}$ at. $\%^{-1}$, whereas the experimental value of Ganne for CuAl lies between $-(1.45\pm0.51)\times10^{-3}$ and $-(1.07\pm0.07)\times10^{-3}$ at. $\%^{-1}$, in the concentration range of 1.06 to 7.55 at. % Al. Given the simplicity of the calculation, we consider the currently calculated results to be in good agreement with the experimental measurements : The sign of $d\beta/\beta dC_i$ is correctly predicted as well as its absolute value, the latter affirmation being viewed within the context of the uncertainties in both the calculated and the measured values. The fact that $\beta_{\text{Al}}>\beta_{\text{Cu}}$, whereas $d\beta/\beta dC_i<0$, clearly negates all models of thermal expansion that treat the alloy as a simple, composite system.

## I. INTRODUCTION

Even for those pure metals and alloy systems for which reliable solvent-solvent and solute-solvent pair potentials are available, the problem of calculating the thermal expansion of these metallic systems is complicated by the volume-dependent forces that inevitably come into play. A recent calculation of the thermal expansion of AlMg and AlCa alloys by Gilder *et al.*[1] reviews the numerous problems encountered in such an approach. In addition, as there are relatively few reliable solvent-solvent and solute-solvent pair potentials available[2] to describe the constituents of most alloy systems, both experimentalist and theorist are usually more than satisfied to, at least, have at their disposition a model that adequately relates one manifestation of the anharmonicity of the interionic potential, namely, the thermal expansion, to another consequence of lattice anharmonicity, such as the third-order elastic constants.

Such a calculation of the thermal expansion of a solid from a knowledge of its third-order elastic constants was originally carried out by Sheard.[3] Using an anisotropic-continuum model of the solid in conjunction with Grüneisen's theory[4] of thermal expansion, Sheard calculated the Grüneisen parameters, or equivalently, the thermal expansion of KCl and NaCl from Lazarus'[5] third-order elastic constant data, and found reasonably good agreement with the experimentally measured values[6] of the thermal expansion of these ionic crystals. Collins[7] was sufficiently encouraged by this approach that he undertook similar calculations for a variety of metals and ionic crystals. In Collins's notation, the Grüneisen parameter $\gamma$ is given by

$$\gamma=\sum_{\vec{q},p}\gamma_{\vec{q},p}C_{\vec{q},p}\Big/\sum_{\vec{q},p}C_{\vec{q},p}\,, \tag{1}$$

where

$$\gamma_{\vec{q},p}=-\left(\frac{\partial\ln\omega_{\vec{q},p}}{\partial\ln V}\right)_T \tag{2}$$

and

$$C_{\vec{q},p}=k_B\left(\frac{\hbar\,\omega_{\vec{q},p}}{k_BT}\right)^2\frac{\exp(\hbar\,\omega_{\vec{q},p}/k_BT)}{[\exp(\hbar\omega_{\vec{q},p}/k_BT)-1]^2}\,. \tag{3}$$

Here $\omega_{\vec{q},p}$ is the frequency of the normal mode described by the wave number $\vec{q}$ and polarization $p$, $C_{\vec{q},p}$ is the constant-volume specific heat associated with this mode, and $V$ is the volume of the crystal. The anisotropic-continuum model assumes that $\omega_{\vec{q},p}=qc_p(\theta,\phi)$, where $c_p(\theta,\phi)$ is the velocity of a sound wave of polarization $p$ propagating in the direction $(\theta,\phi)$. Combining Eqs. (1), (2), and (3), Collins obtained

$$\gamma=\frac{\sum_p\int_\Omega\gamma_p(\theta,\phi)j_4(x_p)x_p^{-3}(\theta,\phi)d\Omega}{\sum_p\int_\Omega j_4(x_p)x_p^{-3}(\theta,\phi)d\Omega}\,, \tag{4}$$

where

$$\gamma_p(\theta,\phi)=\tfrac{1}{3}-\left(\frac{\partial\ln c_p(\theta,\phi)}{\partial\ln V}\right)_T \tag{5}$$

and

$$j_4(x)=\int_0^x u^4 e^u (e^u-1)^{-2}\,du \,. \tag{6}$$

$x_p(\theta,\phi)$ is the ratio of $\Theta_p(\theta,\phi)/T$, where $\Theta_p(\theta,\phi)$ is the Debye temperature for waves of the $p$th branch traveling in the direction $(\theta,\phi)$. Evidently, once having determined $\gamma$ from Eq. (4), the Grüneisen relation $\gamma=\beta V B^T/C_v$ can be used to determine the thermal expansion $\beta$, assuming, of course, that the isothermal bulk modulus $B^T$ is known.

Whereas Sheard solved Quimby and Sutton's[8] cubic equation for $c_p(\theta,\phi)$ on a relatively finely divided angular grid, subsequently using a computer to effect the numerical integrations appearing in Eq. (4) in order to determine $\gamma$, Collins somewhat reduced the numerical complexity of Sheard's procedure by fitting a six-term expansion in cubic harmonics to six selective values (directions of high symmetry) of the integrands appearing in Eq. (4). Although the values of $\gamma$, as well as their temperature variation, were in reasonably good agreement with the corresponding thermal-expansion data, it is obvious that Eq. (4) involves a relatively complicated numerical analysis. Collin's and Sheard's calculations were limited to either pure metals or ionic crystals, inasmuch as experimental values of the third-order elastic constants of alloys were not available at that time.

In 1973, Cain and Thomas[9] (hereafter referred to as CT) used an ultrasonic technique to measure the third-order elastic constants of various dilute CuAl alloys. Using a refinement of Hiki *et al.*[10] of Eq. (4), involving the utilization of Brugger's[11] formulation of the Grüneisen mode parameters, CT predicted the aluminum-concentration dependence of the thermal expansion of their CuAl alloys. They found that $d\beta/\beta dC_i = -3.8\times10^{-3}$ at. %$^{-1}$, where $d\beta$ is the change in the coefficient of thermal expansion of the pure, copper host induced by the introduction of a concentration $dC_i$ of aluminum-impurity atoms. It should be pointed out that the calculation of Hiki *et al.*[10] is numerically nontrivial. It involves a relatively important computer calculation in the symmetry-reduced part of the Brillouin zone involving ~25 000 vibrational modes.

It was until only very recently that the quantity $d\beta/\beta dC_i$ was measured by Ganne[2] in CuAl dilute alloys. Ganne's measurements show that

$$-(1.45\pm0.51)\times10^{-3}\,\text{at.}\%^{-1} \le d\beta/\beta dC_i \le -(1.07\pm0.07)\times10^{-3}\,\text{at.}\%^{-1}$$

for 1.06 at.% $\le C_i \le$ 7.55 at.%. Not having access to the uncertainty in the CT calculated value of $d\beta/\beta dC_i = -3.8\times10^{-3}$ at.%$^{-1}$, it is rather difficult to compare this value with that of Ganne.

The purpose of this paper is to present a simplified model calculation of the thermal expansion of alloys from their third-order elastic constants, within the context of a Debye isotropic continuum, It is, after all, the anisotropic nature of Sheard's solid that is basically responsible for the resultant numerical complexity involved in the determination of $\gamma$. As there is no one unique way to convert a monocrystal to its isotropic "equivalent", the results of a number of "averaging" procedures will be presented. As will be seen, the present calculation can be performed with the equivalent of a TI 59 or HP 67 calculator. In addition, the results are in surprisingly good agreement with Ganne's experimental data, inasmuch as we have calculated the uncertainty in $d\beta/\beta dC_i$ for each averaging procedure due to the experimental uncertainty in the input data. The present work is limited to CuAl, simply because all of the necessary experimental measurements (second- and third-order elastic constants and coefficient of thermal expansion) are available for this alloy. To our knowledge, the only other alloy for which the concentration dependence of the second- and third-order elastic constants have been measured is CuNi. As we are currently in the process of measuring the concentration dependence of the coefficient of thermal expansion of this system, a another test of the present calculational technique will be possible at a future time. In any case, the present model would appear to be applicable to most alloy systems, regardless of the nature of the constituents.

## II. THEORY

### A. Shear-modulus-dependent averaging

In what follows, the differential operator "$d$" will denote the change in any host-crystal property (specified by the subscript "0") induced by the addition of an impurity concentration $dC_i$. Thus, for the nondispersionless host and its associated alloys,

$$\begin{aligned} d\omega/\omega &= dq/q + d\langle c\rangle/\langle c\rangle \\ &= d\langle c\rangle/\langle c\rangle - dL/L \equiv \mu \,, \end{aligned} \tag{7}$$

where $L=V^{1/3}\sim q^{-1}$ and $\langle c\rangle$ is a suitably averaged sound velocity over the longitudinal and transverse vibrational modes of the crystal. In the Debye model of the lattice specific heat of an isotropic solid, $\langle c\rangle$ is given by[13]

$$\langle c\rangle = [(c_l^{-3}+2c_t^{-3})/3]^{-1/3} \,, \tag{8}$$

where $c_l$ and $c_t$ are, respectively, the longitudinal and transverse elastic-wave velocities. According to Eq. (7), all phonon frequencies are fractionally shifted by the same amount $\mu$ due to the impurity concentration $dC_i$, no distinction being made between longitudinal and transverse modes. Using Eq. (5), we can now write the following for the mode-independent $\gamma_0$'s of the host crystal:

$$\frac{\gamma_0}{B_0^T}=\frac{1}{3B_0^T}-\frac{1}{B_0^T}\left(\frac{\partial\ln\langle c_0\rangle}{\partial\ln V_0}\right)_T=\frac{1}{3B_0^T}+\frac{1}{\langle c_0\rangle}\left(\frac{\partial\langle c_0\rangle}{\partial P}\right)_T, \tag{9a}$$

or

$$d\left(\frac{\gamma_0}{B_0^T}\right)=\frac{1}{\langle c_a\rangle}\left(\frac{\partial\langle c_a\rangle}{\partial P}\right)_T-\frac{1}{\langle c_0\rangle}\left(\frac{\partial\langle c_0\rangle}{\partial P}\right)_T+\frac{1}{3}\left(\frac{1}{B_a^T}-\frac{1}{B_0^T}\right), \tag{9b}$$

where the subscript "$a$" refers to the dilute alloy. As, by definition, $dL_0=L_a-L_0$ and $d\langle c_0\rangle=\langle c_a\rangle-\langle c_0\rangle$, differentiating Eq. (7) with respect to pressure $P$ yields

$$\left(\frac{\partial\mu}{\partial P}\right)_T=\frac{\langle c_a\rangle}{\langle c_0\rangle}\left[\frac{1}{\langle c_a\rangle}\left(\frac{\partial\langle c_a\rangle}{\partial P}\right)_T-\frac{1}{\langle c_0\rangle}\left(\frac{\partial\langle c_0\rangle}{\partial P}\right)_T\right]+\frac{L_a}{3L_0}\left(\frac{1}{B_a^T}-\frac{1}{B_0^T}\right). \tag{10}$$

As $\langle c_a\rangle\approx\langle c_0\rangle$ and $L_a\approx L_0$ to a very good approximation, between Eqs. (9) and (10) we then obtain

$$d\gamma_0/\gamma_0-\frac{dB_0^T}{B_0^T}\cong(B_0^T/\gamma_0)\left(\frac{\partial\mu}{\partial P}\right)_T. \tag{11}$$

The quantities $\langle c_{a,0}\rangle^{-1}(\partial\langle C_{a,0}\rangle/\partial P)_T$ appearing in Eq. (10) are evaluated by recourse to Eq. (8). For an isotropic solid, we know that[14]

$$c_l=[(B+4G/3)\rho]^{1/2}\ \text{and}\ c_t=(G/\rho)^{1/2}, \tag{12}$$

where $\rho$ is the crystal density and $B$ and $G$ are the adiabatic bulk and shear moduli, respectively. Substituting Eq. (12) into Eq. (8), and then taking the logarithmic derivative with respect to pressure, we obtain

$$\frac{1}{\langle c\rangle}\left(\frac{\partial\langle c\rangle}{\partial P}\right)_T=-\frac{1}{2B^T}+\frac{\frac{1}{2}(B+4G/3)^{-5/2}(B'+4G'/3)+G^{-5/2}G'}{(B+4G/3)^{-3/2}+2G^{-3/2}}, \tag{13}$$

where $B'\equiv(\partial B/\partial P)_T$ and $G'\equiv(\partial G/\partial P)_T$. Thus, the right-hand side of Eq. (11) is evaluated by recourse to experimental data for the isothermal and adiabatic bulk moduli, as well as the constant-temperature pressure derivatives of the bulk and shear moduli. Differentiating the Grüneisen relation $\gamma=\beta VB^T/C_v$, with respect to $C_i$, and making use of Eq. (11), we obtain

$$\frac{d\beta}{\beta dC_i}=\frac{B_0^T}{\gamma_0 dC_i}\left(\frac{\partial\mu}{\partial P}\right)_T+C_{v0}^{-1}\frac{dC_{v0}}{dC_i}-V_0^{-1}\frac{dV_0}{dC_i}. \tag{14}$$

In the Debye model of the heat capacity of a solid, $C_v=C_v(\Theta_D/T)$. Thus,

$$C_{v0}^{-1}\frac{dC_{v0}}{dC_i}=\frac{\mu}{dC_i}\frac{\Theta_D}{T}\left(C_{v0}^{-1}\frac{\partial C_v(\Theta_D/T)}{\partial(\Theta_D/T)}\right). \tag{15}$$

The term in large round parentheses on the right-hand side of Eq. (15) can be directly obtained from Debye tables[15] of $C_v$ vs $\Theta_D/T$. Equations (10), (13), (14), and (15), together with x-ray, lattice-parameter measurements of the alloy as a function of the impurity concentration $C_i$, evidently permit the calculation of $d\beta/\beta dC_i$. As ultrasonic measurements yield information with regard to the second- and third-order elastic constants of the crystal, the quantity $(\partial\mu/\partial P)_T$ obviously depends on the averaging procedure that establishes the functional relation between $G$, $(\partial G/\partial P)_T$, and $c_{11}$, $c_{12}$, $c_{44}$, $(\partial c_{11}/\partial P)_T$, $(\partial c_{12}/\partial P)_T$, and $(\partial c_{44}/\partial P)_T$ for a crystal of cubic symmetry. These relations are presented in the following sections.

### *1. Voigt and Reuss averaging procedures*

The Voigt[16] averaging technique essentially resides in spatially averaging the elastic constants over all directions. The expression for the Voigt-averaged shear modulus $G_V$ and its pressure derivative $G_V'$, in terms of the second- and third-order elastic constants, are given by

$$G_V=\frac{(2c'+3c_{44})}{5} \tag{16}$$

and

$$\left(\frac{\partial G_V}{\partial P}\right)_T\equiv G_V'=\frac{2c''+3c_{44}'}{5}, \tag{17}$$

where $2c'=(c_{11}-c_{12})$, $2c''=(\partial c_{11}/\partial P)_T-(\partial c_{12}/\partial P)_T$, and $c_{44}'=(\partial c_{44}/\partial P)_T$.

The Reuss[17] method is based on a spatial average of the elastic compliances. The Reuss shear modulus $G_R$ and its pressure derivative $G_R'$ are expressed as follows:

$$G_R=5c'c_{44}/(2c_{44}+3c') \tag{18}$$

and

$$\left(\frac{\partial G_R}{\partial P}\right)_T\equiv G_R'=5[c''c_{44}+c'c_{44}'-c'c_{44}(2c_{44}'+3c'')/(2c_{44}+3c')]/(2c_{44}+3c'). \tag{19}$$

### 2. *Hashin and Shtrikman averaging procedures*

The Voigt and Reuss bounds for the shear modulus were considerably improved by Hashin and Shtrikman.[18] The larger of these bounds is termed the Hashin shear modulus $G_H$, whereas the smaller of the two is referred to as the Shtrikman shear modulus $G_S$. These shear moduli and their pressure derivatives are given by the following expressions:

$$G_H = c_{44} + 2[5/(c'-c_{44}) + 3.6(B+2c_{44})/c_{44}(3B+4c_{44})]^{-1} \equiv c_{44} + 2H^{-1}, \tag{20}$$

$$\begin{aligned} G'_H = c'_{44} + 2H^{-2}[&5(c''+c'_{44})/(c'-c_{44})^2 - 3.6(B'+2c'_{44})/c_{44}(3B+4c_{44}) \\ &+ 3.6(B+2c_{44})c'_{44}/c^2_{44}(3B+4c_{44}) + 3.6(B+2c_{44})(3B'+4c'_{44})/c_{44}(3B+4c_{44})^2], \end{aligned} \tag{21}$$

$$G_S = c' + 3[5/(c_{44}-c') + 2.4(B+2c')/c'(3B+4c')]^{-1} \equiv c' + 3S^{-1}, \tag{22}$$

and

$$\begin{aligned} G'_S = c'' + 3S^{-2}[&5/(c_{44}-c'')/(c_{44}-c')^2 - 2.4(B'+2c'')/c'(3B+4c') \\ &+ 2.4(B+2c')c''/c'^2(3B+4c') + 2.4(B+2c')(3B'+4c'')/c'(3B+4c')^2]. \end{aligned} \tag{23}$$

Evidently, the symbols $H$ and $S$, when not subscripts, represent the second term in square brackets on the right-hand side of Eqs. (20)–(23). Needless to say, regardless of the averaging procedure, the polycrystalline bulk modulus and its pressure derivatives are always given by

$$B = (c_{11} + 2c_{12})/2 \tag{24}$$

and

$$B' = (c'_{11} + 2c'_{12})/3. \tag{25}$$

### B. Debye-temperature-dependent averaging

Ledbetter and Naimon[19] proposed an averaging procedure based on the assumption that the Debye temperature of the polycrystalline aggregate is equal to that of the monocrystal. According to de Launay,[20] the Debye temperature $\Theta_D$ of a cubic crystal is related to the crystal's elastic constants as follows:

$$\begin{aligned} \Theta_D^{-3} = (4\pi\Omega k_B^3 \rho^{3/2}/9h^3)\{&(c_{12}+2c_{44})^{-3/2}[1 - 1.8(c'-c_{44})/(c_{12}+2c_{44}) \\ &+ (189c_{12} + 173c_{44})(c'-c_{44})^2/70(c_{12}+c_{44})(c_{12}+2c_{44})^2] \\ &+ 2c_{44}^{-3/2}[1 - 0.6(c'-c_{44})/c_{44} + (35c_{12}+43c_{44})(c'-c_{44})^2/70(c_{12}+c_{44})c^2_{44}]\}. \end{aligned} \tag{26}$$

However, in Debye's model of the specific heat of an isotropic continuum, $\langle c \rangle$ is related to $\Theta_D$ in the following way[13]:

$$\Theta_D^{-3} = (4\pi k_B^3 \Omega)/(3h^3 \langle c \rangle^3). \tag{27}$$

By eliminating $\Theta_D^{-3}$ between Eqs. (26) and (27), we obtain a relation between $\langle c \rangle$, $c_{11}$, $c_{12}$, $c_{44}$, and $\rho$. Again taking the logarithmic derivative of $\langle c \rangle$ with respect to pressure, we obtain

$$\langle c \rangle^{-1}\left(\frac{\partial \langle c \rangle}{\partial P}\right)_T = \langle c \rangle^{-1}\left(\frac{\partial \langle c \rangle}{\partial P}\right)_T (c', c_{12}, c_{44}, c'', c'_{12}, c'_{44}). \tag{28}$$

Given the complexity of Eq. (26), the explicit form of the right-hand side of Eq. (28) is not given because of its considerable length.

In any case, the calculation of $d\beta/\beta dC_i$ proceeds in exactly the same way for both Debye-temperature- and shear-modulus-type averaging: Eqs. (28) and (13) are used to evaluate $\langle c \rangle^{-1}(\partial \langle c \rangle/\partial P)_T$, which is then injected into Eq. (10). Equations (11) and (14) then yield $d\beta/\beta dC_i$, since $\langle c \rangle$, and hence $\mu$, is calculated as well for each alloy concentration. Thus, Eq. (15) determines the second term on the right-hand side of Eq. (14), and recourse to lattice-parameter data for the alloy system in question allows the determination of the last term (the size effect) of Eq. (14).

## III. RESULTS

### A. Treatment of alloy data

The input data to the present calculation are indicated in Table I. The values of $c'_{11}$, $c'_{12}$, $c'_{44}$, $c''$, and $B'$ (Ref. 9) were measured at the concentrations indicated. The pressure derivatives for pure copper, indicated as well, had been previously obtained by Hiki and Granato.[21] As the elastic-constant and density measurements of Cain and Thomas[22] had not been performed on alloys having the same aluminum concentration as those used

TABLE I. Elastic-constant and density-input data as a function of aluminum-impurity concentration.

| $C_i$ (at.%) | $\rho$ (kg/m$^3$) | $c_{12}$ (Mbar) | $c_{44}$ (Mbar) | $c'$ (Mbar) | $B$ (Mbar) | $c'_{12}$ | $c'_{44}$ | $c''$ | $B'$ |
|---|---|---|---|---|---|---|---|---|---|
| 0.0 | 8938.4 | 1.219 | 0.754 | 0.237 | 1.377 | 5.190 | 2.63 | 0.375 | 5.44 |
| 3.1 | 8725.3 | 1.216 | 0.764 | 0.231 | 1.370 | 4.900 | 2.452 | 0.545 | 5.264 |
| 5.6 | 8551.9 | 1.213 | 0.769 | 0.225 | 1.363 | 4.895 | 2.421 | 0.544 | 5.258 |
| 7.4 | 8426.5 | 1.207 | 0.774 | 0.222 | 1.355 | 4.903 | 2.395 | 0.536 | 5.260 |

for the third-order elastic constant measurements, the values of $c_{11}$, $c_{12}$, $c_{44}$, $c'$, $B$, and $\rho$ appearing in Table I were obtained by linear interpolation. Although the experimental uncertainties of the measured quantities of Table I are not indicated, a detailed discussion of their order of magnitude and their important impact on the calculated values of $d\beta/\beta dC_i$ is presented in the following section.

### B. Currently calculated values of $d\beta/\beta dC_i$

The currently calculated values of $d\beta/\beta dC_i$ are given in Table II as a function of $C_i$ for each of the averaging procedures previously discussed. Here, $C_i$ is not the aluminum concentration of a particular alloy, but rather the average concentration of the neighboring alloy states of Table I used in the calculation. For example, the concentration $C_i = 4.35$ at.% appearing in Table II means that $d\beta/\beta dC_i$ corresponding to this concentration was calculated from the alloys Cu-3.1-at.% Al and Cu-5.6-at.% Al (see Table I). In other words, the pure host state previously referred to in Eqs. (9), (10), (11), (14), and (15) in practice is, in fact, synonymous with any alloy state whose concentration is changed by $dC_i$. Inasmuch as the alloy data of Table I correspond to concentrations of 0, 3.1, 5.6, and 7.4 at.%, $d\beta/\beta dC_i$ is calculated at average aluminum concentrations of 1.55, 4.35, and 6.5 at.%.

TABLE II. Calculated values of $d\beta/\beta dC_i$ as a function of averaging procedure and aluminum concentration.

| Averaging procedure | $d\beta/\beta dC_i$ ($10^{-3}$ at.%$^{-1}$) $C_i$ (at.%) 1.55 | 4.35 | 6.50 |
|---|---|---|---|
| Reuss | +64 | $+0.2\pm 2$ | $-7.3\pm 6.0$ |
| Shtrikman | +26 | $-3.3\pm 1.7$ | $-8.8\pm 4.1$ |
| Hashin | +1.6 | $-5.5\pm 1.4$ | $-9.7\pm 2.6$ |
| Voigt | $-13$ | $-7.7\pm 2.1$ | $-11.0\pm 3.8$ |
| de Launay | $-13$ | $-7.7\pm 2.2$ | $-11.0\pm 3.9$ |

Three remarks are in order concerning the calculated values of $d\beta/\beta dC_i$ shown in Table II. First of all, regardless of the concentration, $d\beta/\beta dC_i$ decreases systematically as we pass successively through the Reuss, Shtrikman, Hashin, and Voigt averaging procedures. For CuAl, there is apparently no difference between Voigt- and Debye-temperature-(de Launay) type averaging. Second of all, the ensemble of the calculations indicates that the sign of $d\beta/\beta dC_i$ is negative. The uncertainty in $d\beta/\beta dC_i$, where indicated, varies from 1000% to 25%, with 25–35% being the most probable uncertainty. Third of all, the uncertainties are not indicated for $C_i = 1.55$ at.% because we have very little confidence in the pure-copper data as used in the present context, simply because the contribution of the unpinned dislocations in the pure-copper specimens is absent in the CuAl alloys where the dislocations are pinned by the aluminum impurities. The present calculations thus place $d\beta/\beta dC_i$ between $+(0.2\pm 2)\times 10^{-3}$ at.% and $-(11\pm 4)\times 10^{-3}$ at.%$^{-1}$.

A few remarks are in order concerning the relatively large uncertainties in the calculated values indicated in Table II. These uncertainties are due to the experimental uncertainty in each input quantity to the calculation. Concerning these latter uncertainties, Cain and Thomas[22] claim that $c_{11}$, $c_{44}$, and $c'$ are measured to ±0.001 Mbar, whereas $c_{12}$ and $B$ have a probable error of ±0.002 Mbar. Although it is not indicated in their article, we estimate that their densities are measured to ±0.1 kg/m$^3$. With regard to the uncertainties in the pressure derivatives of the elastic constants, they apparently depend on the concentration of the alloy: for $3.1 \text{ at.\%} \leqslant C_i \leqslant 7.4 \text{ at.\%}$, $0.002 \leqslant \delta B' \leqslant 0.013$, $0.001 \leqslant \delta c'' \leqslant 0.008$, $0.001 \leqslant \delta c'_{44} \leqslant 0.005$, $0.002 \leqslant \delta c'_{12} \geqslant 0.017$, and $0.002 \leqslant \delta c'_{11} \leqslant 0.008$. Thus, for example, to evaluate the uncertainty in the first two terms on the right-hand side of Eq. (14), each input quantity, in turn, is changed by an amount corresponding to its error bar while all the other quantities are fixed at their nominal values. The changes in the calculated quantity corresponding to these changes in the input data are then summed in a reasonably statistical way. The relative importance of each input datum to the uncertainty in the first and second terms of Eq. (14) depends on the averaging procedure being used as well as the concentration of the alloy. However, our calculations indicate that the uncertainty in $c_{44}$ and $c'$ plays an important role in each of the averaging procedures in determining the uncertainty in the first term of Eq. (14). The uncertainty in $c''$ would appear to be next in importance.

As concerns the second term of Eq. (14), the major contribution to its uncertainty comes from the uncertainties in $c_{44}$ and $c'$, $\rho$ and $B$ playing a very minor role. The uncertainty in this term is typically ~15%. Inasmuch as $C_{c0}^{-1}dC_{v0}/dC_i$ is usually no greater than about a tenth of $(B_0^T/\gamma_0)(\partial\mu/\partial P)_T$, its uncertainty obviously contributes little to the overall uncertainty in $d\beta/\beta dC_i$.

The last term of Eq. (14), $V_0^{-1}dV_0/dC_i$, is calculated from the lattice-parameter data of Obinate and Wasserman.[23] Their data indicate that $V_0^{-1}dV_0/dC_i = (2.20 \pm 0.06)\times 10^{-3}$ at.%$^{-1}$ within the currently considered concentration range. As $V_0^{-1}dV_0/dC_i$ rarely exceeds ~40% of $(B_0^T/\gamma_0)(\partial\mu/\partial P)_T$, it is rather obvious that the predominant uncertainty in $d\beta/\beta dC_i$ has its origin in the large uncertainty in $(B_0^T/\gamma_0)(\partial\mu/\partial P)_T$. For instance, for $C_i = 4.35$ at.% in the Hashin averaging procedure

$$\begin{aligned} d\beta/\beta dC_i &= -(3.0 \pm 1.3)\times 10^{-3} \\ &\quad -(0.33 \pm 0.05)\times 10^{-3} - (2.20 \pm 0.06)\times 10^{-3} \\ &= -(5.5 \pm 1.4)\times 10^{-3}\ \text{at.}\%^{-1}. \end{aligned}$$

Reference to the CT (Ref. 9) third-order elastic-constant data shows that the data for Cu-7.4-at.% Al have uncertainties markedly greater than those of the pressure derivatives measured for alloys corresponding to $C_i = 3.1$ and 5.6 at.%. An obvious manifestitation of the relatively poor quality of the $C_i = 7.4$-at.% data is apparent in the size of the error bars of the third column of Table II: they are approximately twice as large as those of the second column. It is for this reason that we consider the calculated values of $d\beta/\beta dC_i$ corresponding to $C_i = 4.35$ at.% statistically more significant than those associated with $C_i = 6.5$ at.%. Inasmuch as the uncertainties in $d\beta/\beta dC_i$ for $C_i = 4.35$ at.% are nevertheless too large to discern significant differences between the averaging procedures employed, we feel that the most statistically significant value of $d\beta/\beta dC_i$ emerging from the present calculation corresponds to the arithmetic average of the calculated values appearing in the second column of Table II. This yields $d\beta/\beta dC_i = -(4.8 \pm 2.9)\times 10^{-3}$ at.%$^{-1}$.

It should be pointed out that in both Eqs. (13) and (14), $B$ was used in place of $B^T$. We have verified that this introduces an uncertainty in the calculated value of $d\beta/\beta dC_i$ never exceeding 0.2%.

## IV. DISCUSSION OF RESULTS AND CONCLUSIONS

The currently calculated values of $d\beta/\beta dC_i$ are indicated in Fig. 1, along with the CT calculated value and the experimental values of Ganne. The present results are obviously in good agreement with the CT, anisotropic-continuum value of $-3.8 \times 10^{-1}$ at.%$^{-1}$.

The currently calculated value of $d\beta/\beta dC_i = -(4.8 \pm 2.9)\times 10^{-3}$ at. %$^{-1}$, as well as that of CT, is based on the room-temperature values of the second- and third-order elastic constants, whereas the data of Ganne correspond to $T \sim 140$ K. Given this difference in temperature between the measured and currently calculated values of $d\beta/\beta dC_i$, as well as the size of the error bars in the present calculation, we consider that the present model is in reasonably good agreement with the experimental measurements.

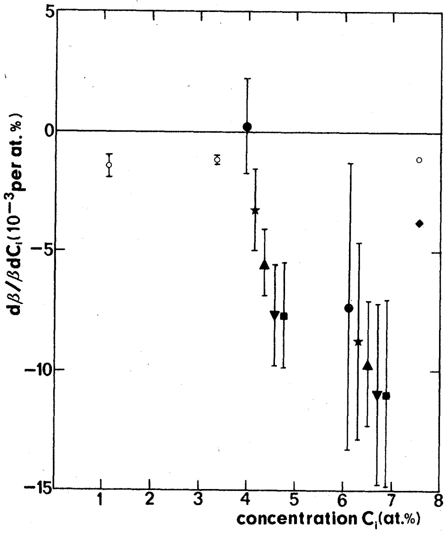

FIG. 1. Calculated and experimental values of $d\beta/\beta dC_i$ as a function of aluminum concentration $C_i$ for CuAl alloys. In the present model, the averaging procedures are represented as follows: Reuss (●), Shtrikman (★), Hashin (▲), Voigt (▼), de Launay (■). The currently calculated values at 4.35 and 6.50 at. % are indicated as clusters centered at these concentrations for the sake of clarity. The CT (Ref. 9) calculated point (◆) is based on alloy data spanning the aluminum concentration interval of 3.1 to 10.8 at. %, and is thus placed at $C_i = 7.5$ at. %. The experimental points (○) are those of Ganne (Ref. 12). The error bar of the experimental point at $C_i = 7.55$ at. % is equal to the diameter of the open circle.

The present isotropic-continuum model, as well as the anisotropic-continuum model used by Cain and Thomas, both predict the correct sign and order of magnitude of $d\beta/\beta dC_i$. We consider this to be a nonnegligible accomplishment, in view of the fact that the alloy is treated as a dispersionless medium. There is both theoretical[24] and experimental[25] evidence that indicates that for certain solids there is a considerable difference between the Grüneisen parameters of high- and low-dispersion phonons. In addition, the present model obviously ignores the possible contribution of local modes in the CuAl system. Although there is experimental evidence[26] for the existence of localized modes in CuAl, their Grüneisen parameters have not been either measured or estimated.

The sign of the measured and calculated values of $d\beta/\beta dC_i$ should, once and for all, destroy all illusions regarding the utility of those models[27,28] that treat the alloy as a simple, composite system. These models essentially assert that the solute has the same physical properties whether or not it is dissolved in the solvent. Inasmuch as $\beta_{Al} > \beta_{Cu}$,[29] these models would predict $d\beta/\beta dC_i > 0$, just the opposite of what is actually observed.

Finally, it should be emphasized that model calculations of alloy thermal expansion, whether they be isotropic or anisotropic, are extremely sensitive to the second- and third-order elastic-constants data used. Although the second- and third-order elastic constants used in the present calculation are accurate to $\sim 10^{-3}$, this uncertainty is unfortunately large enough to induce uncertainties of typically 25–35% in the calculated values of $d\beta/\beta dC_i$.

## ACKNOWLEDGMENTS

The authors are extremely grateful to Dr. Quêrê of the C.E.A., Fontenay-aux-Roses, for many stimulating discussions as well as his constant encouragement throughout this work. We are indebted to both the Centre d'Etudes Nucléaires (C.E.A.), France, and the Centre National de Recherche Scientifique (C.N.R.S.), France, for their joint support of this project.

---

[1] H. M. Gilder, M. Asty, and Ph. Audit, preceding paper, Phys. Rev. B 22, 5613 (1980).

[2] L. Dagens, M. Rasolt, and R. Taylor, Phys. Rev. B 11, 2726 (1975).

[3] F. W. Sheard, Philos. Mag. 3, 1381 (1958).

[4] E. Grüneisen, Handb. Phys. 10, 1 (1926).

[5] D. Lazarus, Phys. Rev. 76, 545 (1949).

[6] B. Dayal, Proc. Indian Acad. Sci. Sect. A 20, 145 (1944).

[7] J. G. Collins, Philos. Mag. 8, 323 (1963).

[8] S. L. Quimby and P. M. Sutton, Phys. Rev. 91, 1122 (1953).

[9] L. S. Cain and J. F. Thomas, Jr., Phys. Rev. B 8, 5372 (1973).

[10] Y. Hiki, J. F. Thomas, Jr., and A. V. Granato, Phys. Rev. 153, 764 (1967).

[11] K. Brugger, Phys. Rev. 137, A1826 (1965).

[12] J. P. Ganne, J. Phys. (Paris) Lett. 40, L-481 (1979).

[13] L. Brillouin, *Wave Propagation in Periodic Structures* (Dover, New York, 1953), p. 163.

[14] N. F. Mott and H. Jone, *The Theory of the Properties of Metals and Alloys* (Dover, New York, 1958), p. 3

[15] *Handbuch der Physik* (Springer, Berlin, 1926), Vol. 10, p. 367.

[16] W. Voigt, *Lehrbuch der Krystallphysik* (B. G. Teubner, Leipzig, 1928), p. 962.

[17] A. Reuss, Z. Angew. Math. Mech. 9, 49 (1929).

[18] Z. Hashin and S. Shtrikman, J. Mech. Phys. Solids 10, 343 (1962).

[19] H. M. Ledbetter and E. R. Naimon, J. Appl. Phys. 45, 66 (1974).

[20] J. de Launay, J. Chem. Phys. 21, 1975 (1953).

[21] Y. Hiki and A. V. Granato, Phys. Rev. 144, 411 (1966).

[22] L. S. Cain and J. F. Thomas, Jr., Phys. Rev. B 4, 4245 (1971).

[23] I. Obinata and G. Wasserman, Naturwissenschaften 21, 382 (1933).

[24] R. Taylor and H. R. Glyde, J. Phys. F 6, 1915 (1976).

[25] J. Meyer, G. Dolling, J. Kalus, G. Vettier, and J. Paureau, J. Phys. F 6, 1899 (1976).

[26] R. M. Nicklow, P. R. Vijayaraghavan, H. G. Smith, and M. K. Wilkinson, Phys. Rev. Lett. 20, 1245 (1968).

[27] P. S. Turner, J. Res. Nat. Bur. Stand. 37, 239 (1946).

[28] T. J. Hughes and J. C. Brittain, Phys. Rev. A 135, 1738 (1964).

[29] F. R. Kroeger and C. A. Swenson, J. Appl. Phys. 48, 853 (1977).