

**Calculation of the intrinsic coefficient of thermal expansion of spherical, coherent inclusions:
Application to Al-Ag, Fe-Cu, and Ni-Al**

H. M. Gilder

*Laboratoire Léon Brillouin, Centre d'Etudes Nucléaires Saclay,
91191 Gif-sur-Yvette Cedex, France*

(Received 19 May 1981)

With the use of the definition of the intrinsic coefficient of thermal expansion (ICTE) β_d of a point defect, and in consideration of the Eshelby-calculated change in matrix volume caused by the appearance of an inclusion as the inclusion's volume of formation, the calculation of the ICTE of spherical, coherent inclusions is effected. It is found that β_d/β , where β is the CTE of the matrix, can grow very large ($\beta_d/\beta \gg 1$) as a direct result of the singular nature of the temperature derivative of the matrix-inclusion contact stress for nearly equal values of the matrix and inclusion lattice parameters. It is precisely in this domain that the tool presently used to treat the problem, linear elastic theory, has its greatest validity. The model is applied to three real alloy systems, two of which, Al-Ag, and Fe-Cu, contain Guinier-Preston zones, whereas the third, Ni-Al, contains γ' precipitates. β_d/β is found to be -5.2 , $+150$, and -18 for Al-Ag, Fe-Cu, and Ni-Al, respectively. In addition, the easily measurable predicted isothermal change in matrix volume caused by the precipitates in Al-Ag and Ni-Al indicates the important role that dilatative properties can play in the experimental determination of precipitate-growth kinetics. The present calculation shows that the absolute value of the ICTE of atomically large, spherical, Eshelby-type coherent inclusions can, as for point defects, considerably exceed that of the matrix, and under certain conditions can attain values that dwarf those of point defects.

I. INTRODUCTION

It is reasonably safe to say that in recent years both theory and experiment have shown that defects, such as the vacancy¹⁻³ and impurity⁴ in metallic systems, can sometimes possess strikingly large intrinsic coefficients of thermal expansion: $|\beta_d|/\beta \gg 1$, where β_d is the intrinsic coefficient of thermal expansion (ICTE) associated with the defect formation volume ΔV_d [$\beta_d = \Delta V_d^{-1}(\partial \Delta V_d / \partial T)_p$], and β is the coefficient of thermal expansion (CTE) of the matrix. $|\beta_d/\beta| \gg 1$ for point defects is more than a mere curiosity. Not only does this condition have extremely interesting consequences in the theory of Arrhenius-plot curvature,⁵ but it represents, as well, an additional parameter against which interatomic potentials in alloys can be tested.⁴

The question that naturally arises is whether large ICTE's are to be expected for only defects of strictly atomic dimensions (point defects), or whether atomically large defects such as coherent

inclusions, can equally well exhibit such extraordinary dilatative properties. We attempt to provide an answer to this question in the present article by calculating the ICTE of a spherical, coherent inclusion by means of linear elastic theory. In other words, expressions are derived for β_d/β in the context of Eshelby's model⁶ of a coherent inclusion.

In Eshelby's model it is assumed that the matrix and inclusion are perfectly elastic, isotropic, continuous media described by different elastic constants, lattice parameters, and, we might add, coefficients of thermal expansion. The inclusion is the result of some process that transforms a part of the matrix into precipitated material. Thus, the state of stress and strain of the system can be understood by cutting around the region which is to transform and removing it from the matrix. After the unconstrained transformation takes place (accompanied by a homogeneous deformation), surface tractions are applied in order to restore the region to its original form, thus allowing it to be put back in the hole in the matrix. It is welded to the

matrix along the interface thus formed. In relaxing to its equilibrium configuration, the system changes its volume by an amount ΔV_d , the formation volume of the defect, or coherent inclusion in the present case. Since this sequence of operations can be performed at any temperature T it is obvious that $\Delta V_d = \Delta V_d(T)$. Thus, Eshelby's formulation of ΔV_d is the starting point for the present calculation.

The purpose of this paper, then, is to derive an expression for β_d/β in terms of the various physical parameters that define the equilibrium state of the matrix-inclusion system, and to see under what conditions $|\beta_d/\beta| \gg 1$. The impact of this inequality on measurable changes in the dilatative properties of the matrix is subsequently explored for three real systems in which spherical, coherent precipitates form, and for which the data defining the necessary physical parameters of the matrix and inclusion are available. In particular, results are presented for the alloys Al—4.5 at. % Ag and Fe—1.1 at. % Cu, in which the precipitated coherent inclusions are Guinier-Preston zones, and for the alloy Ni—12.71 at. % Al, in which the coherent inclusions are γ' precipitates.

The calculation is developed for spherical, coherent inclusions in order to avoid the attendant complexity that would inevitably make the physics less apparent for coherent precipitates of more complicated shape (disks or plates, for instance). As we shall see in Sec. IV A, it is precisely the small difference in atomic volume between the matrix and inclusion that is responsible for the spectacular values of β_d/β currently calculated. On the other hand, it is generally acknowledged^{7,8} that a small difference in volume, being equivalent to a small strain energy, favors the formation of spherical precipitates. Thus, it is reasonably safe to say that the orders of magnitude of some of the dilatative properties currently calculated for spherical inclusions would probably change for disks or plates, but this would obviously need to be confirmed at some future time by the appropriate calculations.

II. THEORY

A. Eshelby's model of the coherent inclusion and its extension to the determination of β_d/β

Figure 1 shows the various physical and geometrical parameters that define the matrix (spherical hollow shell) and the inclusion (solid

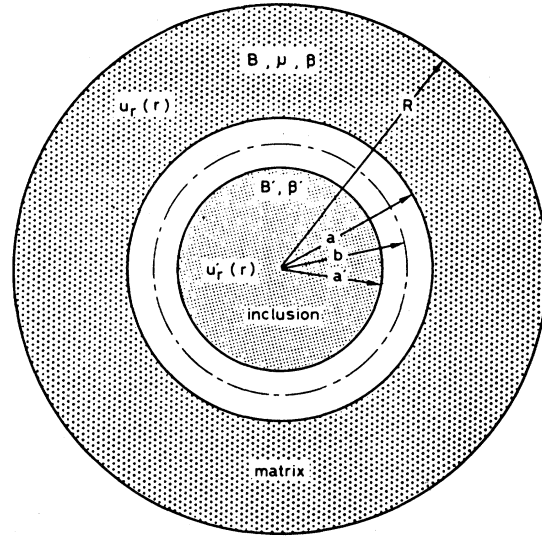


FIG. 1. The various physical and geometrical parameters defining the expanding Eshelby coherent inclusion. The matrix is described by bulk (B) and shear (μ) moduli, coefficient of thermal expansion (β), elastic displacement [$u_r(r)$], and inner (a) and outer (R) radii. The inclusion by bulk modulus (B'), coefficient of thermal expansion (β'), elastic displacement [$u'_r(r)$], and radius (a'). The matrix-inclusion interface by radius (b).

sphere). The unconstrained, post-transformation radius of the inclusion is denoted by a' , whereas its pretransformation radius, or equivalently, the radius of the hole cut in the matrix, is denoted by a . B and μ are the bulk and shear moduli, respectively, of the matrix, and B' is the bulk modulus of the inclusion. The "expanding" version of the Eshelby inclusion is obviously described, as well, by the CTE's of the matrix (β) and the inclusion (β').

After the inclusion is "welded" to the matrix the interface assumes the "relaxed" position defined by the radial distance $r = b$. Eshelby's method of calculating the change in volume ΔV_d of the system due to this relaxation is extremely straightforward. As the details are given elsewhere,^{6,9} suffice it to say that because of the spherical symmetry, the elastic displacement is a particularly simple function of r : $u_r(r) = fr^{-2} + gr$ in the matrix and $u'_r(r) = hr$ in the inclusion. The constants f , g , h , and b are then easily determined by means of the boundary conditions: $u_r(a) = b - a$, $u'_r(a') = b - a'$, $\sigma_{rr}(a) = \sigma'_{rr}(a')$, and $\sigma_{rr}(R) = 0$. The third condition ensures that the interface is in equilibrium under the action of the radial stresses in the matrix (σ_{rr}) and the inclusion (σ'_{rr}), while the fourth con-

dition ensures that the outer surface ($r=R$) is in a stress-free state. Since $\Delta V_d = 4\pi R^2 u_r(R)$, Eshelby then obtained (but in a different form) the following expression for ΔV_d :

$$\Delta V_d = (4\pi a^3/3)[(\eta+1)/B]\sigma_{rr}(a), \quad (1a)$$

where

$$(\sigma_{rr}(a) = 3B'(a'/a - 1)/(B'\eta/B + a'/a) \quad (1b)$$

and $\eta = 3B/4\mu$. Since both the inclusion and matrix are assumed to be isotropic in this model, μ is hereafter taken as the Voigt-averaged shear modulus for simplicity. Now ΔV_d is nothing more than the formation volume of the inclusion, so that differentiating Eq. (1) with respect to temperature T at constant pressure we obtain the following, sought-after expression for β_d/β :

$$\beta_d/\beta = 1 + \beta^{-1} \frac{d}{dT} \ln[(\eta+1)/B] + \beta^{-1} \frac{d}{dT} \ln \sigma_{rr}(a), \quad (2)$$

where

$$\begin{aligned} \beta^{-1} \frac{d}{dT} \ln \sigma_{rr}(a) &= \beta^{-1} \left[B'^{-1} \frac{dB'}{dT} \right] \\ &+ \frac{a'}{3a} (1 - \beta'/\beta) \\ &\times \left[\frac{1}{1 - a'/a} + \frac{1}{B'\eta/B + a'/a} \right] \\ &- \frac{\beta^{-1}}{B'\eta/B + a'/a} \frac{d}{dT} (B'\eta/B). \end{aligned} \quad (3)$$

Since the number of atoms is conserved during the transformation that converts a part of the matrix to inclusion, a and a' are proportional to the matrix and inclusion lattice parameters, respectively. Inasmuch as β_d/β is a function of a'/a , a and a' can be considered as lattice parameters for all intents and purposes.

B. Size of the various terms contributing to β_d/β for real systems

The maximum strain in the system occurs at the matrix-inclusion interface, and is $\sim |a - a'|/a$. Pure metals and alloys typically have yield-point strains $\sim 10^{-3}$ (Ref. 10) and $\eta \sim 2$,¹¹ so that $(1 - a'/a)^{-1} \gg (B'\eta/B + a'/a)^{-1}$, even for $B'/B = 0$. Thus, Eq. (3) becomes, to a very good

approximation

$$\begin{aligned} \beta^{-1} \frac{d}{dT} \ln \sigma_{rr}(a) &= \beta^{-1} \left[B'^{-1} \frac{dB'}{dT} \right] + \frac{1}{3} \left[\frac{1 - \beta'/\beta}{1 - a'/a} \right] \\ &- \frac{\beta^{-1}}{B'\eta/B + 1} \frac{d}{dT} (B'\eta/B). \end{aligned} \quad (4)$$

It is difficult, if not impossible, to further simplify Eqs. (2) and (4) without loss of generality. This becomes obvious when we estimate the order of magnitude of each of the terms appearing in them. Since, typically,

$$B^{-1} dB/dT \sim \mu^{-1} d\mu/dT \sim -100 \times 10^{-6} \text{ K}^{-1}$$

(Ref. 11) and $\beta \sim 50 \times 10^{-6} \text{ K}^{-1}$,¹² then

$$\begin{aligned} \left| \beta^{-1} \frac{d}{dT} \ln[(\eta+1)B] \right| &\sim \left| \beta^{-1} \left[B'^{-1} \frac{dB'}{dT} \right] \right| \\ &\sim \left| \frac{\beta^{-1}}{B'\eta/B + 1} \frac{d}{dT} (B'\eta/B) \right| \\ &\sim 2-3. \end{aligned}$$

The remaining term,

$$M(\beta'/\beta, a'/a) \equiv \frac{1}{3} \frac{1 - \beta'/\beta}{1 - a'/a},$$

can, on the other hand, assume a very wide range of both positive and negative values. We notice that M is the term that explicitly takes into account the "misfit" between the lattice parameter of the inclusion and that of the matrix.

We can estimate a most probable lower bound for M by assuming that the precipitate has the same crystallographic structure as the matrix, but at a slightly different composition. For simplicity, consider a binary alloy for which the difference in fractional solute concentration between the matrix and precipitate is denoted by ΔC . Then,

$$|M|_{\min} \sim \left| \lim_{\Delta C \rightarrow 0} M \right|.$$

Under these conditions

$$M \equiv \frac{1}{3} \frac{1 - \beta'/\beta}{1 - a'/a} \rightarrow \frac{\Delta\beta/\Delta C}{\beta\Delta V_d/\Omega}, \quad (5)$$

where $\Delta\beta \equiv \beta' - \beta$, Ω is the average atomic volume of the matrix and $\Delta V_d/\Omega = (3/\Delta C)(a' - a)/a$. Typically, for dilute binary alloys, $|\Delta\beta/\Delta C| \sim 7 \times 10^{-5} \text{ K}^{-1}$.⁴ As $|\Delta V_d/\Omega| \sim 1$ for substitutional impurities,¹³ Eq. (5) yields $|M|_{\min} \sim 1$. In reality, M can easily dwarf this

lower limit by at least an order of magnitude, as will be seen in what follows.

III CALCULATION OF β_d/β FOR COHERENT PRECIPITATES IN REAL SYSTEMS

A. Guinier-Preston zones

Let us first consider the case of coherent, Guinier-Preston (GP) zones that precipitate in certain age-hardening alloys. For instance, in the alloy Al-4.5 at. % Ag, certain aging conditions can give rise to GP zones in the form of silver spheres embedded in a matrix containing no more than 1 at. % Ag.¹⁴ Inasmuch as the average diameter of the GP zones is of the order of 70 Å, we are justified in using the ordinary bulk properties of silver to describe the zones. With regard to the matrix, the situation is slightly more complicated in that there are currently no published data available for the CTE nor for the bulk and shear moduli of Al-1 at. % Ag. However, as the terms of Eqs. (2) and (4) need only be estimated to the order of 10% for the purposes of the present discussion, we can consider the matrix to be composed of pure aluminum. This can be justified by treating the silver atoms as "Eshelby" inclusions embedded in a pure alumi-

num continuum. Within this context it can easily be shown⁹ that

$$\Delta\mu/\mu\Delta C \cong \Delta B/B\Delta C = \left[\frac{1-B/B'}{a'/a-1} \right] \frac{\Delta a}{a\Delta C}, \quad (6)$$

where ΔB and $\Delta\mu$ are the changes in the bulk and shear moduli, respectively, of the pure matrix caused by the introduction of the fractional concentration of "atomic" inclusions ΔC . Using the data of Table I in conjunction with Eq. (6), we find that $\Delta B_{280\text{ K}} = \Delta B_{300\text{ K}} = 4.2 \times 10^{-4}$ Mbar to much better than 1%. Since $\Delta a/a\Delta C = \Delta V_d/3\Omega$, the value of $\Delta a/a\Delta C = 19 \times 10^{-6}/\text{at. \%}$ measured¹³ at 300 K is used at 280 K as well: Even if ΔV_d were to vary 100 times faster than Ω with temperature, over a 20-K interval, $\Delta a/a\Delta C$ would change by no more than $100\beta\Delta T/3 = 4.5\%$. Thus, since $\Delta B \ll B_{\text{Al}}$ and $d\Delta B/dT \ll dB_{\text{Al}}/dT$, $B_{\text{matrix}} = B_{\text{Al}}$ and $(B^{-1}dB/dT)_{\text{matrix}} = (B^{-1}dB/dT)_{\text{Al}}$, to a very good approximation. The same argument and conclusion obviously hold for the shear modulus μ as well.

The misfit term M can be evaluated exactly since the lattice parameter and its variation with temperature have been measured¹³ for Al-1 at. % Ag. Nevertheless, the measurements indicate that $a_{\text{matrix}} = a_{\text{Al}}$, and $\beta_{\text{matrix}} = \beta_{\text{Al}}$, to an excellent ap-

TABLE I. Reference data used in the present calculation.

System	Components	T (K)	B^a (Mbar)	B'^a (Mbar)	$\mu_V^{a,b}$ (Mbar)	β (10^6 K^{-1})	β' (10^6 K^{-1})	a (Å)	a' (Å)	
Al-Ag	Al	280	0.7641		0.2643	68 ^c		4.0477 ^e		
		300	0.7609		0.2613		4.0495 ^e			
	Ag	280		1.0418		57 ^c		4.0846 ^e		
		300		1.0378			4.0862 ^e			
Fe-Cu	Fe	280	1.6825		0.9062	34 ^c		2.8662 ^e		
		300	1.6799		0.9023					
	Cu	280		1.3753		49 ^c			2.8690 ^{e,f}	
		300		1.3708						
Ni-Al	Ni-12 at. % Al	300				41.4 ^d		3.5465 ^g		
	Ni ₃ Al	300					29.4 ^d	3.5649 ^g		

^aReference 11.

^b μ_V is the Voigt-averaged value of μ : $\mu_V = (c_{11} - c_{12} + 3c_{44})/5$.

^cReference 12.

^dReference 19.

^eReference 13.

^f $a = a_{\text{Cu}}/2^{1/3}$ since α -Fe is bcc and Cu is fcc.

^gReference 18.

proximation for our purposes.

The data appearing in Table I are used to calculate each of the terms appearing in Eqs. (2) and (4). The results are shown in Table II. We notice, referring to the last column, that $\beta_d/\beta = -5.2$. Furthermore, since $a'/a > 1$, it can be seen from Eqs. (1a) and (1b) that $\Delta V_d > 0$. Thus, as temperature increases, the GP-zone formation volume astonishingly contracts about five times faster than the matrix expands. The formation of GP zones, in this case, decreases the apparent average lattice anharmonicity of the system.

A much more startling case, however, involves the Fe-1.1 at. % Cu alloy. Under certain aging conditions⁸ the GP zones are composed of essentially pure copper, and are spherical with an average diameter of about 100 Å. Even though there are currently no data available for the CTE and the bulk and shear moduli of the Fe-1 at. % Cu matrix, the same arguments, based on Eq. (6) and the data of Table I, used for the Al-1 at. % Ag system can again be invoked to show that $B_{\text{matrix}} = B_{\text{Fe}}$, $(B^{-1}dB/dT)_{\text{matrix}} = (B^{-1}dB/dT)_{\text{Fe}}$, $a_{\text{matrix}} = a_{\text{Fe}}$, and $\beta_{\text{matrix}} = \beta_{\text{Fe}}$. Using $a_{\text{Fe}} = 2.8662$ Å, $a_{\text{Cu}} = 2.8690$ Å (refer to the explanatory note in Table I), $\beta_{\text{Fe}} = 34 \times 10^{-6} \text{ K}^{-1}$, and $\beta_{\text{Cu}} = 49 \times 10^{-6} \text{ K}^{-1}$, we find that $1 - a'/a = -9.8 \times 10^{-4}$ and $M = 150$. Table II clearly shows this to be the dominant term in Eqs. (2) and (4): $\beta_d/\beta \approx 150$. Thus, as astounding as that would appear, the volume of formation of the GP zone in Fe-1.1 at. % Cu expands about 150 times faster than the matrix: The GP zone increases the apparent average lattice anharmonicity of the system.

B. γ' precipitates

As a final example we consider the precipitation hardenable Ni-12.71 at. % Al alloy. In this sys-

tem certain aging conditions¹⁵ give rise to the random nucleation of coherent, cuboid-shaped particles. These γ' (Ni₃Al) precipitates have a Cu₃Au-type ordered structure¹⁶ and a lattice parameter and elastic constants which are very closely equal to those of the surrounding matrix.¹⁷ With $B' \approx B$ and $\mu' \approx \mu$, Eqs. (2) and (4) can be considerably simplified to yield the following expression for β_d/β :

$$\beta_d/\beta \approx 1 + \frac{1}{3} \frac{1 - \beta'/\beta}{1 - a'/a} \quad (7)$$

For the alloy Ni-12.71 at. % Al, the data of Phillips¹⁸ indicate that $1 - a'/a \sim -5 \times 10^{-3}$ at room temperature. From the thermal expansion data of Kornilov and Mints¹⁹ it is found that the room-temperature CTE increases from $29.4 \times 10^{-6} \text{ K}^{-1}$ for Ni₃Al to $41.4 \times 10^{-6} \text{ K}^{-1}$ for Ni-12.71 at. % Al. Thus, Eq. (7) yields $\beta_d/\beta = -18$. Since $\Delta V_d > 0$ [refer to Eq. (1)], the presence of the γ' precipitate decreases the apparent average lattice anharmonicity of the alloy in an obviously extremely efficient way.

IV. DISCUSSION OF RESULTS

A. The singular nature of the misfit term M

The various contributions to β_d/β appearing in Table II for the three systems considered above indicate that $|\beta_d/\beta| \gg 1$ is a direct consequence of $|M| \gg 1$. The precipitation-matrix misfit term M can obviously acquire very large absolute values for $a' \approx a$ and $\beta' \neq \beta$.

It is obvious that this condition can be realized in a binary alloy whose constituents have almost identical atomic volumes and whose precipitated phase is monatomic. When such a situation arises

TABLE II. Terms contributing to β_d/β .

System	E_M^a	E_P^b	E_{MP}^c	$1 - \beta'/\beta$	$1 - a'/a$	M	β_d/β
Al-4.5 at. % Ag	+ 6.7	-2.8	-4.2	+ 0.16	-9.1×10^{-3}	-5.9	-5.2
Fe-1.1 at. % Cu	+ 4.6	-4.8	-0.8	-0.44	-9.8×10^{-4}	+ 150	+ 150
Ni-12.71 at. % Al				+ 0.29	-5.2×10^{-3}	-19	-18

$$^a E_M \equiv \beta^{-1} \frac{d}{dT} \ln[(\eta + 1)/B].$$

$$^b E_P \equiv \beta^{-1} (B'^{-1} dB'/dT).$$

$$^c E_{MP} \equiv - \frac{\beta^{-1}}{B'\eta/B + 1} \frac{d}{dT} (B'\eta/B).$$

it is extremely unlikely that $\beta' \approx \beta$, inasmuch as the interatomic potential and its anharmonic component vary considerably from one element to another. Under these conditions the singularity that appears in M as $a' \rightarrow a$ cannot be suppressed by the finite difference that persists between β' and β . Referring to Tables I and II, we notice that such is the case for the Fe-Cu system, and to a much lesser degree for the Al-Ag system.

As concerns the Ni-Al system, the large differences in composition (~ 12 at. % Al) and degree of order between the γ' precipitate and the matrix contribute to a relatively large value of M . It is by no means simple, nor is it essential in the present context to give a detailed explanation of this state of events. However, we note in passing that, in general, the CTE of an alloy changes much more rapidly than the lattice parameter as the composition is varied. In Al-1.1 at. % Mg, for instance, recent data⁴ indicate that $d\beta/\beta dC \approx 0.74$, whereas $da/adC \approx 0.12$ in the range 100–200 K. This means that β changes about 6 times faster than a as the magnesium concentration is varied. As shown in Table II, for the Ni-Al system, $|(d\beta/\beta)/(da/a)| \sim 50$, indicating that the local change in the degree of order is just, if not perhaps more important than the local change in composition in determining M , and hence β_d/β .

Again referring to Table II, for the three systems under consideration, $|1 - \beta'/\beta|$ varies between relatively narrow limits, whereas $|1 - a'/a|$ changes by an order of magnitude. Since $|M| \sim 5$ for $|1 - a'/a| \sim 10^{-2}$, the condition $a' \approx a$ is obviously not restrictive enough to ensure $|M| \gg 1$. However, it would appear that for typical values of β encountered for metals, and based on the present results, $|1 - a'/a| \leq 2 \times 10^{-3}$ would appear sufficient to ensure $|M|$, $|\beta_d/\beta| \gg 1$. It should be emphasized that it is precisely in the domain where linear elastic theory is valid ($|1 - a'/a| \ll 1$) that M , and hence β_d/β become singular.

As concerns the sign of β_d/β , it is the same as the sign of M for $|M| \gg 1$. The sign of M , in turn, depends on β'/β as well as a'/a . Thus, although an inclusion may expand faster than its surrounding matrix with increasing temperature ($\beta'/\beta > 1$), β_d/β can be negative as long as the lattice parameter of the inclusion exceeds that of the matrix ($a'/a > 1$). For $|M| \sim 1$, no one term of Eqs. (2) and (4), in general, dominates β_d/β , so that the sign of β_d/β is a complicated function of all of the parameters describing the inclusion and the matrix.

B. β_d/β and observable effects

β_d/β is only one of a number of factors controlling the physically significant quantity $\delta\beta/\beta$, the fractional change in the CTE of the alloy caused by the appearance of coherent inclusions throughout its volume. In fact, it can easily be shown⁵ that $\delta\beta/\beta$ is related to the normalized defect CTE, β_d/β , the normalized defect volume $\Delta V_d/\Omega$, and the concentration C_i of inclusions in the following way:

$$\delta\beta/\beta = C_i(\Delta V_d/\Omega)(\beta_d/\beta - 1) \quad (8a)$$

or

$$\delta\beta/\beta \approx C_i(\Delta V_d/\Omega)(\beta_d/\beta) \quad \text{for } \beta_d/\beta \gg 1. \quad (8b)$$

Equation (8b) is obviously appropriate for the systems currently under consideration. Since ΔV_d is given by Eqs. (1a) and (1b), the quantity $\Delta V_d/\Omega$ appearing in Eq. (8b) is evaluated by replacing the factor $(4\pi/3)a^3$ of Eq. (1a) by Ω . With regard to C_i , depending on the alloy system being studied, it is either taken directly from previous measurements or calculated from published data involving the density of inclusions ρ_i (inclusions per volume), or equivalently the average inter-inclusion distance S_i , and the average diameter D_i of the inclusions. Thus,

$$C_i = \pi D_i^3 \rho_i / 6 = (\pi/6)(D_i/S_i)^3. \quad (9)$$

Ultimately, $\delta\beta/\beta$ is judged to be large or small depending upon whether the change in length δL that it induces between a sample containing inclusions and an inclusion-free dummy can be detected for a reasonable change δT of the sample-dummy system temperature. If the sample and dummy have the same initial length L_0 , then

$$\delta L = L_0 \delta T \delta\beta / 3. \quad (10)$$

Equations (8b), (1b), (9), and (10) are used to calculate $\delta\beta/\beta$ from its various components, as well as δL . The results are shown in Table III and are based on the data appearing therein (columns 2–4) as well as those of Table I. The values of δL are based on conservative values of L_0 and δT : $L_0 = 4$ cm and $\delta T = 100$ K ($250 \leq T \leq 350$ K).

We notice that Fe-Cu has the largest value of β_d/β , yet the smallest value of $\delta\beta$, hence δL , of the three systems considered. We see that this is due to the cumulative effects of an extremely small concentration of GP zones combined with a relatively feeble value of $\Delta V_d/\Omega$. As the overall precision in differential-length measurement by optical

TABLE III. Various parameters contributing to measurable thermal effects in alloy systems containing coherent inclusions.

System	D_i (Å)	S_i (Å)	ρ_i (cm ⁻³)	C_i	$\Delta V_d/\Omega$	β_d/β	$\delta\beta/\beta$	$\delta\beta$ (K ⁻¹)	$ \delta L $ ^d (μm)
Al-Ag	70 ^a		2×10^{17} ^a	36×10^{-3}	30×10^{-3}	-5.2	-6.7×10^{-3}	-4.5×10^{-7}	0.6
Fe-Cu	100 ^b	1500 ^b		1.2×10^{-3}	2.7×10^{-3}	+150	$+4.9 \times 10^{-4}$	$+1.7 \times 10^{-8}$	0.02
Ni-Al				57×10^{-3} ^c	15×10^{-3}	-18	-1.6×10^{-2}	-6.6×10^{-7}	0.9

^aReference 23, p. 800.

^bReference 8.

^cReferences 15 and 16.

^d δL based on a gauge length of 4 cm and a temperature excursion of 100 K centered at room temperature.

means is typically⁴ $\sim 10^{-2}$ μm, the change in CTE due to the presence of the inclusions is barely detectable in the case of Fe-Cu, whereas it is easily measurable in the case of Al-Ag and Ni-Al.

C. $\Delta V_d/\Omega$ and growth kinetics of coherent precipitates

The formation of coherent precipitates changes the initial volume of the alloy by an amount $C_i(t)\Delta V_d$, where $C_i(t)$ is the volume fraction of inclusions resulting from growth during a time t at an aging temperature T_G . The associated change in length $\delta L_G(t)$ is given by

$$\delta L_G(t) = [L_G \Delta V_d(T_G) / 3\Omega(T_G)] C_i(t), \quad (11)$$

where L_G is the initial length of the alloy at the temperature T_G . Equation (11) obviously suggests the possibility of determining the growth kinetics of the precipitates through the measurement of $\delta L_G(t)$, and hence $C_i(t)$.

Burke²⁰ pointed out some years ago that dilatometry could be used to measure the kinetics of phase transformations in metals. We can use Eq. (11) and the previously calculated quantities appearing in Table III to demonstrate the extremely good sensitivity of this technique.

Reference to Table III shows that for Al-Ag and Ni-Al, $\delta L_G(\infty) \sim 13$ μm for $L_G = 4$ cm, so that $0 < \delta L_G(t) \lesssim 13$ μm for these two systems. The resolution ($\sim 10^{-2}$ μm) afforded by optical-interferometric, differential-length measurement is clearly more than sufficient to accurately determine $\delta L_G(t)$ and $d\delta L_G(t)/dt$ during the precipitation process. For precipitates having a definite, time-independent composition, $C_i(t)$ is the only time-dependent term on the right-hand side of Eq.

(11). This allows a relatively straightforward interpretation of $\delta L_G(t)$. Isothermal length measurement, under these conditions, would then appear to be an interesting complement to x-ray small-angle-scattering and resistivity measurements whose interpretation is relatively complicated,^{21,22} and to direct measurements of precipitate growth parameters by electron microscopy, whose realization is not without considerable experimental effort.^{8,23}

To the knowledge of this author, the one attempt that appears in the literature to use length measurements (but nondifferential) in this way was made²⁴ with respect to γ' precipitation in austenitic stainless steels. Although the interpretation of the results was not clear cut due to the complexity of the alloy systems studied, it is nevertheless interesting to note that the fractional length change ($\sim 10^{-4}$) is the same order of magnitude as that currently calculated ($13 \mu\text{m}/4 \text{ cm} \sim 10^{-4}$) for Al-Ag and Ni-Al.

A final word is in order concerning the possible application of Eqs. (10) and (11) to the determination of the average diameter $\langle D_i \rangle$ of a precipitate. For two samples of the same alloy having the same value of C_i but different values of $\langle D_i \rangle$, δL and δL_G will be the same because $\Delta V_d/\Omega$ is independent of the absolute size of the precipitate [see Eq. (1)]. Complementary information regarding ρ_i must obviously be available in order to say something about $\langle D_i \rangle$.

D. Similarities between dilative properties of coherent inclusions and atomic point defects

As mentioned in Sec. I, measured values of $|\beta_d/\beta|$ for vacancies and impurities in metals lie

in the range $1 \lesssim |\beta_d/\beta| \lesssim 20$. The present results indicate that although $(\beta_d/\beta)_{CI}$ can be positive or negative for coherent inclusions (CI), just as for point defects (PD), $|(\beta_d/\beta)_{CI}|$ can, in contrast to $|(\beta_d/\beta)_{PD}|$, attain values as high as ~ 150 .

As it is well known that atomic point defects have formation volumes typically $\sim \Omega$ and melting-point concentrations $\sim 10^{-3}$, the present results for spherical, coherent inclusions in Al-Ag and Ni-Al indicate that $(\Delta V_d/\Omega)_{PD}/(\Delta V_d/\Omega)_{CI} \sim 50$ and $(C_i)_{CI}/(C_i)_{PD} \sim 50$. This means that although there are generally large differences between their concentrations and formation volumes, both point defects and inclusions generally produce about the same fractional change in system volume: $(C_i \Delta V_d/\Omega)_{PD} \sim (C_i \Delta V_d/\Omega)_{CI} \sim 10^{-3}$.

As concerns the concentration-normalized change in the CTE $\delta\beta/C_i$, we notice from Table III that although $\delta\beta$ for Fe-Cu is about 30 times smaller than that for Al-Ag or Ni-Al, for all three systems

$$|(\delta\beta/C_i)_{CI}| \sim 1.2 \times 10^{-5} \text{ K}^{-1}.$$

Since, typically,

$$|(\delta\beta/C_i)_{PD}| \sim 7 \times 10^{-5} \text{ K}^{-1}$$

(see Sec. III), it would appear that to within a factor of 5, $|(\delta\beta/C_i)_{PD}| \sim |(\delta\beta/C_i)_{CI}|$.

Thus, it would seem reasonable to say that although point defects and coherent inclusions appear to differ radically with respect to their equilibrium concentrations and formation volumes, the measurable effects that they produce concerning changes in system volume and CTE are about the same.

V. CONCLUSIONS

The present model calculation of the ICTE β_d of spherical, coherent inclusions shows that $|\beta_d|$ can become very much greater than β of the matrix as a direct result of the singular nature of the

temperature derivative of the matrix-inclusion contact stress that varies as $(1-a'/a)^{-1}$ in the limit $a'/a \rightarrow 1$. It is precisely in this domain where β_d/β becomes singular that linear elastic theory is valid as a tool for treating the problem.

Three real alloy systems in which spherical, coherent precipitates form as a result of certain aging conditions are explored in the context of the present ideas. In particular, associated with the Guinier-Preston zones in Al-Ag and Fe-Cu, β_d/β is found to be -5.2 and $+150$, respectively. In the third system investigated, Ni-Al, in which γ' precipitates of ordered Ni_3Al form, $\beta_d/\beta = -18$. In spite of the enormous value of β_d/β in Fe-Cu, the changes induced in matrix volume and CTE by the inclusion are the smallest of those calculated for the systems considered, owing to the relatively small zone-formation volume and concentration in this system. On the other hand, the easily measurable value of these changes in Al-Ag and Ni-Al signals the important role that dilatative properties can play in the experimental determination of precipitate growth kinetics.

Finally, the present calculation shows that the absolute value of the ICTE of atomically large, spherical, Eshelby-type coherent inclusions can, as for point defects, considerably exceed that of the matrix, and under certain conditions can even attain values that dwarf those of point defects.

ACKNOWLEDGMENTS

The author is indebted to both the Commissariat à l'Énergie Atomique (C.E.A.), France and the Centre National de Recherche Scientifique (C.N.R.S.), France, for their joint support of this work. The author is extremely grateful to Dr. Lambert and Dr. Mériel of Léon Brillouin and to Dr. Lesueur of the Centre d'Études Nucléaires (C.E.A.) for their critical reading of the manuscript.

¹L. C. Chhabildas and H. M. Gilder, Phys. Rev. B **5**, 2135 (1972).

²J. P. Ganne and J. von Stebut, Phys. Rev. Lett. **43**, 634 (1979).

³Ph. Audit and H. M. Gilder, Phys. Rev. B **18**, 4151 (1978).

⁴H. M. Gilder, M. Asty, and Ph. Audit, Phys. Rev. B **22**, 5613 (1980).

⁵H. M. Gilder and D. Lazarus, Phys. Rev. B **11**, 4916 (1975).

⁶J. D. Eshelby, in *Advances in Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York,

- 1956), Vol. 3, p. 79.
- ⁷F. R. N. Nabarro, Proc. R. Soc. London 175, 519 (1940).
- ⁸E. Hornbogen, Acta Metall. 10, 525 (1962).
- ⁹See, for example, Y. Quéré, *Défauts Ponctuels dans les Métaux* (Masson, Paris, 1967), p. 28.
- ¹⁰E. O. Hall, *Yield Point Phenomena in Metals and Alloys* (MacMillan, London, 1970).
- ¹¹G. Simmons and H. Wang, *Single Crystal Elastic Constants and Calculated Aggregate Properties* (MIT, Cambridge, Mass., 1971).
- ¹²*Handbook of Chemistry and Physics*, 36th ed. (Chemical Rubber, Cleveland, 1954).
- ¹³W. B. Pearson, *Handbook of Lattice Spacings and Structure of Metals and Alloys*, (Pergamon, London, 1967), Vol. 2.
- ¹⁴C. S. Barrett and T. B. Massalski, *Structure of Metals*, 3rd ed. (Pergamon, Oxford, 1980), p. 504.
- ¹⁵V. A. Phillips, Acta Metall. 14, 1533 (1966).
- ¹⁶M. Hansen, *Constitution of Binary Alloys*, 2nd ed. (Mc Graw-Hill, New York, 1958), p. 118.
- ¹⁷K. Ono and R. Stern, Trans. Metall. Soc. AIME 245, 171 (1969).
- ¹⁸V. A. Phillips, Philos. Mag. 16, 103 (1967).
- ¹⁹I. I. Kornilov and R. S. Mints, Dok. Acad. Nauk SSSR 88, 5 (1953); 88, 829 (1953).
- ²⁰J. Burke, *The Kinetics of Phase Transformations in Metals* (Pergamon, Oxford, 1965), p. 37.
- ²¹C. Radomsky and H. Löffler, Phys. Status Solidi A 50, 123 (1978).
- ²²J. Mimault, J. Delafond, A. Junqua, A. Naudon, and J. Grilhe, Philos. Mag. B 38, 3, 255 (1978).
- ²³G. Thomas, in *Electron Microscopy and Strength of Crystals*, edited by G. Thomas and J. Washburn (Interscience, New York, 1963).
- ²⁴D. Raynor and J. M. Silcock, Scr. Metall. 2, 399 (1968).