PHYSICAL REVIEW VOLUME 135, NUMBER 6A 14 SEPTEMBER 1964

Theoretical Analysis of the Effect of Substitutional Point Defects on Thermal Expansion*

T. J. Hughes and J. O. Brittain
Materials Science Department, Northwestern University, Evanston, Illinois

(Received 9 April 1964)

A thermal-expansion theory has been derived for primary solid-solution binary alloys treating the solute atoms as elastic spheres imbedded in an infinite elastic continuum and considering the interactions between the thermal expansion of these point defects and the matrix. The theory predicts that the thermal-expansion coefficient of the alloy can be determined from the thermal-expansion coefficients and the elastic constants of the constituents, and from the atomic volume of the solute atom. The theory is verified for various alloys in the temperature and composition ranges consistent with the assumptions of the theory; i.e., for temperature and composition ranges which obey the Grueneisen law of thermal expansion for the pure components and for the alloy.

INTRODUCTION

No adequate theory exists which provides a useful equation relating the thermal expansion of solid-solution alloys to the thermal expansion of the pure constituents. Guertler observed that for binary two-phase alloys the thermal expansion of most alloys is simply the average of the thermal expansion of the respective constituents.[1] However, this behavior is not observed for solid-solution alloys. Nix and MacNair tested the validity of the Grueneisen equation of thermal expansion for Al, Fe, Ni, Cu, and Au and found excellent agreement over a wide temperature range, excepting the range of the Curie transformation in Ni and Fe.[2] Then Nix and MacNair made the assumption that if the constants in the Grueneisen equation for pure materials were additive, the thermal-expansion coefficient of a solid-solution alloy of these materials could be obtained.[3] Checking this assumption for Cu-Au alloys, they found excellent agreement except in the region of the order-disorder transformation of Cu_3Au. However, this treatment by Nix and MacNair was semiempirical and they made no attempt to justify it on theoretical grounds. The present paper is an attempt to provide a comprehensive theory of the thermal expansion in the primary solid-solution region of binary alloys based upon elastic theory and the thermal expansion of the pure constituents.

THEORETICAL TREATMENT

Thermal expansion is a phenomenon which arises from the asymmetry of the vibrational energy versus atomic separation curve. From Fig. 1 it is clear that a rise in temperature from T_1 to T_2 causes an increase in vibrational energy, which forces the atoms to increase their vibrational amplitude from A_1B_1 to A_2B_2 with a corresponding increase in atomic separation from R_1 to R_2. Thus, a temperature increment ΔT has caused an expansion ΔR. Hence, if two elements have different vibrational energy-atom separation curves, a given temperature change ΔT will cause different changes in the atomic amplitudes of vibration. Consequently, in a solid solution of these elements, the solute atoms will vibrate with amplitudes different from those of the solvent atoms. The interaction of these vibrations as temperature changes will result in a thermal expansion of the alloy which is a function of the concentration of substitutional point defects (solute atoms) and the degree to which their vibrational amplitude differs from that of the matrix atoms (solvent atoms). With this in mind, our theory rests on two assumptions:

1. The observed volume coefficient of thermal expansion $\bar{\alpha}_v$ is the sum of $\bar{\alpha}_m$, the matrix thermal-expansion coefficient modified by the effect of the defects upon the expansion of the matrix; and $\bar{\alpha}_d$, the defect expansion coefficient modified by the effect of the matrix on the expansion of the defects.
2. The defect can be treated as an elastic sphere im-

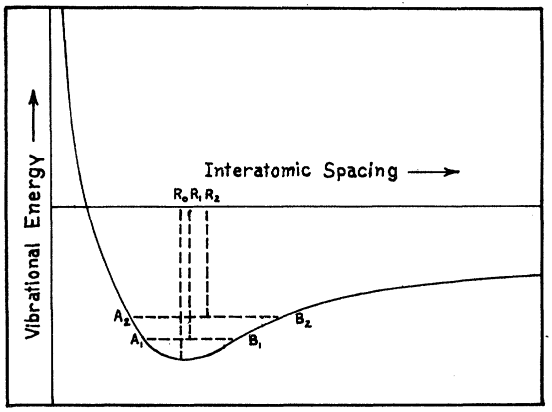

Fig. 1. Change of vibrational energy with interatomic spacing. The amplitudes of vibration are exaggerated.

---

* This research was partly supported by the U. S. Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command and by a Walter P. Murphy fellowship. This paper is based in part on a thesis submitted by T. J. Hughes in partial fulfillment of the requirements for the degree of Master of Science at Northwestern University.

[1] W. Guertler, *Metalltechnischer Kalender, 1922* (Gebrüder Borntraeger, Berlin, 1926), p. 118.

[2] F. C. Nix and D. MacNair, Phys. Rev. **60**, 597 (1941).

[3] F. C. Nix and D. MacNair, Phys. Rev. **60**, 320 (1941).

bedded in an infinite elastic continuum, resulting in an axially symmetrical stress distribution about the defect.

Since thermal expansion is elastic strain, a temperature increment ΔT produces elastic strains ϵ_{ij} in the material. We can determine the volume coefficient of thermal expansion $\bar{\alpha}_v$ by integrating the strains ϵ_{ij} over the volume V of the material. By definition,

$$\bar{\alpha}_v=\frac{1}{\Delta T}\iiint \epsilon_{ij}\delta_{ij}dV \Big/ \iiint dV . \quad i, j=1, 2, 3. \tag{1}$$

Here $\delta_{ij}=1$ for $i=j$, and $\delta_{ij}=0$ for $i\neq j$. Since the thermal-expansion tensor α_{ij} is a symmetrical second-rank tensor, we can write the strain tensor ϵ_{ij} in terms of the principal strains, $\epsilon_{ii}=\epsilon_{11}+\epsilon_{22}+\epsilon_{33}$.

Applying assumption 1, Eq. (1) becomes

$$\begin{aligned}\bar{\alpha}_v&=\bar{\alpha}_m+\bar{\alpha}_d\\ &=\frac{1}{\Delta T}\left[\iiint(\epsilon_{11}+\epsilon_{22}+\epsilon_{33})dV \Big/ \iiint dV\right]_m\\ &\quad+\frac{1}{\Delta T}\left[\iiint(\epsilon_{11}+\epsilon_{22}+\epsilon_{33})dV \Big/ \iiint dV\right]_d .\end{aligned} \tag{2}$$

The combination of different atomic size and different amplitude of vibration between solute and solvent atoms results in an "effective size" difference which creates stresses in the matrix surrounding each solute point defect. Thus, for a temperature change ΔT, the dilatational strain ϵ_{ii} in the alloy has two components: (a) a Hookian component due to stresses created by "effective size" difference between defect and matrix atoms, and (b) a thermal component due to the change in the vibrational amplitude of the atoms.

Analytically, these two components to the dilatational strain ϵ_{ii} for the matrix and for the defect are

$$(\epsilon_{ii})_m=((1-2\nu_m)/E_m)(\sigma_{ii})_m+3\alpha_m\Delta T \tag{3a}$$

$$(\epsilon_{ii})_d=((1-2\nu_d)/E_d)(\sigma_{ii})_d+3\alpha_d\Delta T . \tag{3b}$$

Here E_m, ν_m, α_m, and E_d, ν_d, α_d are Young's modulus, Poisson's ratio, and the linear thermal-expansion coefficient of the pure matrix and defect materials, respectively. (The volume thermal-expansion coefficients are $3\alpha_m$ and $3\alpha_d$.)

Applying assumption 2, we can use Timoshenko's equations relating the principal stresses to the pressure P_m on the matrix due to the spherical defect.[4]

$$\sigma_{11}=\sigma_r=-(R/r)^3P_m \tag{4a}$$

$$\sigma_{22}=\sigma_{33}=\sigma_t=\tfrac{1}{2}(R/r)^3P_m . \tag{4b}$$

Here, σ_r is the radial stress, σ_t is the tangential stress, R is the defect radius, and r is a radius such that $r\geq R$.

Also, from assumption 2, no shear stresses act on the defect. Therefore the maximum shear stress $\tau_{\max}$ is zero, and the maximum shear stress criterion for the defect yields

$$\tau_{\max}=\tfrac{1}{2}(\sigma_{11}-\sigma_{33})=0 . \tag{5}$$

Therefore, $\sigma_{11}=\sigma_{33}$, and since the pressure exerted by the matrix on the spherical defect is $-P_d$ the stresses inside the defect are

$$\sigma_{11}=\sigma_r=-P_d , \tag{6a}$$

$$\sigma_{22}=\sigma_{33}=\sigma_t=-P_d . \tag{6b}$$

We can now obtain the dilatational strain in the matrix by substituting Eqs. (4) into Eq. (3a) and the dilatational strain in the defect by substituting Eqs. (6) into Eq. (3b):

$$(\epsilon_{11}+\epsilon_{22}+\epsilon_{33})_m=3\alpha_m\Delta T \tag{7a}$$

$$(\epsilon_{11}+\epsilon_{22}+\epsilon_{33})_d=((1-2\nu)_d/E_d)(-3P_d)+3\alpha_d\Delta T . \tag{7b}$$

Substituting Eqs. (7) into Eq. (2) we have for unit volume

$$\bar{\alpha}_v=3\alpha_m\iiint_m dV-\frac{3}{\Delta T}\left(\frac{1-2\nu_d}{E_d}\right)\times\iiint_d P_d dV+3\alpha_d\iiint_d dV . \tag{8}$$

To determine P we apply the boundary conditions that, at $r=R$, the pressure on the matrix P_m equals the pressure on the defect P_d, and the displacement of the matrix U_m equals the displacement of the defect U_d. The displacement equations can be written in terms of the pressure P at the matrix-defect interface by means of the principal stress equations, (4) and (6), for σ_r and σ_t.

$$\begin{aligned}U_m=R\epsilon_t&=R\{(1/E_m)[\sigma_t-\nu_m(\sigma_r+\sigma_t)]+\alpha_m\Delta T\}\\ &=R[((1+\nu_m)/2E_m)P+\alpha_m\Delta T]\end{aligned} \tag{9a}$$

$$\begin{aligned}U_d=R\epsilon_t&=R\{(1/E_d)[\sigma_t-\nu_d(\sigma_r+\sigma_t)]+\alpha_d\Delta T\}\\ &=R[((1-2\nu_d)/E_d)(-P)+\alpha_d\Delta T] .\end{aligned} \tag{9b}$$

Equating U_m with U_d and solving for P yields

$$P=\frac{(\alpha_d-\alpha_m)\Delta T}{[(1+\nu_m)/2E_m]+[(1-2\nu_d)/E_d]} . \tag{10}$$

Since we have assumed unit volume of material, if ρ_d is the point-defect concentration per unit volume, and V_d is the volume of one point defect,

$$\iiint_m dV=1-\rho_d V_d , \tag{11a}$$

$$\iiint_d dV=\rho_d V_d . \tag{11b}$$

---

[4] S. Timoshenko and J. N. Goodier, *Theory of Elasticity* (McGraw-Hill Book Company, Inc., New York, 1951), p. 358.

Substituting Eqs. (10) and (11) into Eq. (8),

$$\bar{\alpha}_v = 3\alpha_m(1-\rho_d V_d) - 3\left[\frac{((1-2\nu_d)/E_d)}{((1+\nu_m)/2E_m)+((1-2\nu_d)/E_d)}\right] \times(\alpha_d-\alpha_m)\rho_d V_d + 3\alpha_d\rho_d V_d. \qquad (12)$$

The linear coefficient of thermal expansion $\bar{\alpha}_l$ is, upon setting $\bar{\alpha}_l = \frac{1}{3}\bar{\alpha}_v$ and rearranging terms,

$$\bar{\alpha}_l = \alpha_m - A\rho_d V_d(\alpha_m - \alpha_d)$$

$$A = \frac{((1+\nu_m)/2E_m)}{((1+\nu_m)/2E_m)+((1-2\nu_d)/E_d)}. \qquad (13)$$

This equation, then, predicts the thermal-expansion coefficient for a solid-solution binary alloy from the thermal-expansion coefficients, Young's moduli, and Poisson's ratios of the pure constituents. From the assumptions made in the derivation, this equation would have the following limitations:

1. It should only apply to isotropic alloys since the stress distribution was assumed to be axially symmetrical.
2. It should apply to relatively dilute alloys since the theory ignores interactions between point defects.
3. It should apply only to alloys and temperature ranges in which no solid-state transformations occur, since such transformations involve processes not considered in the theory.
4. It should apply for alloy temperatures approaching the melting point of the lowest melting constituent only if the temperature variation of the elastic constants is known. At still higher temperatures the nature of all of the equation constants change, and the equation cannot be used.

VERIFICATION OF THE THEORY

In testing the theory for various isotropic alloys formed from fcc, bcc, and hcp constituents, we found agreement to be within experimental error for most alloys and temperature ranges compatible with the limitations of the theoretical model. Figure 2 shows the comparison between our theory and the excellent thermal-expansion data for Cu-Au alloys obtained by Nix and MacNair.[3] They found that up to 50°C, the alloys exhibited Grueneisen thermal expansion. Above this temperature the Cu$_3$Au order-disorder transformation disrupted the normal thermal expansion so that their data coincided with the Grueneisen curve only at 250 and 725°C. Thus, from Fig. 2 we see that our theory is in excellent experimental agreement when thermal expansion exhibits normal Grueneisen behavior.

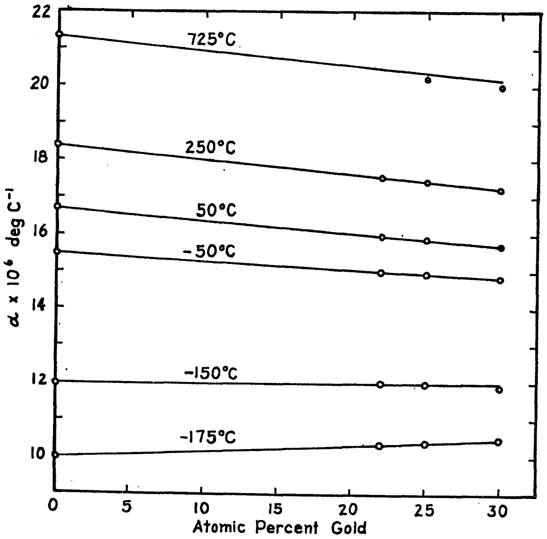

FIG. 2. Thermal expansion in copper gold alloys. Theoretical curve is shown by solid lines.

Figure 3 compares our theoretical curves with experimental curves for the α brasses.[5] In this phase, no transformations occur which would disrupt normal thermal-expansion behavior. However, α brasses are alloys composed of a cubic and a hexagonal metal. Agreement is best at low solute concentrations and improves with increasing temperature, at least up to 250°C. This is 76% of the melting point of zinc, and is the highest temperature for which data is reported. Surprisingly, agreement is still good up to the phase boundary at 37 at.% Zn. This indicates that the stresses around each point defect are short range and, therefore, we were substantially justified in neglecting interactions between point defects.

Thermal-expansion data are limited for solid-solution alloys in which no transformations occur. However, data are available for various commercial solid solution

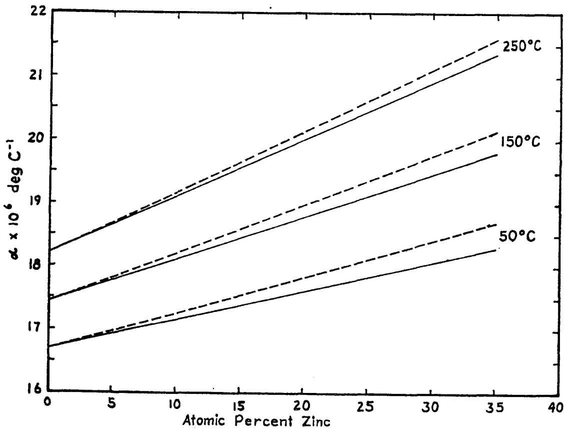

FIG. 3. Thermal expansion in α-brass alloys. Theoretical curve is shown by solid lines. Experimental curve is shown by broken lines.

---

[5] *Metals Handbook*, 8th edition (American Society for Metals, Metals Park, Ohio, 1961), Vol. 1.

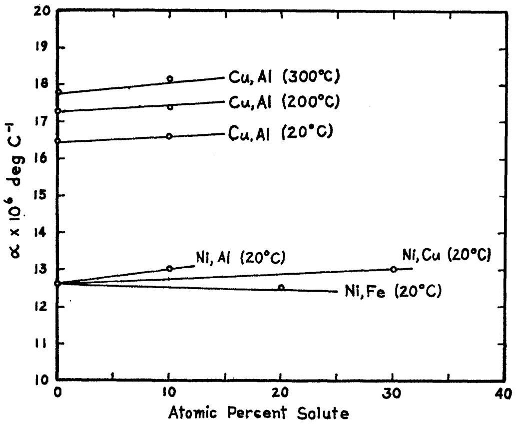

FIG. 4. Thermal expansion of various alloys. Theoretical curve is shown by solid lines.

TABLE II. Equation constants of various alloys.[a]

Alloy	A	V_d
Cu–Au	0.730	1.15×10^{-23} cm^3
Cu–Ni	0.737	0.80×10^{-23} cm^3
Cu–Al	0.414	1.23×10^{-23} cm^3
Ni–Cu	0.895	0.88×10^{-23} cm^3
Cu–Ni	0.527	0.80×10^{-23} cm^3
Cu–Zn	0.530	0.99×10^{-23} cm^3
Ni–Fe	0.610	0.84×10^{-23} cm^3
Fe-Ni	0.603	0.80×10^{-23} cm^3
Ni–Al	0.286	1.23×10^{-23} cm^3
Al–Mg	0.465	1.79×10^{-23} cm^3
Ni–Cr	0.656	0.82×10^{-23} cm^3
Fe–Al	0.290	1.23×10^{-23} cm^3

[a] The first element in the alloy is the solvent. Hence, in Cu–Ni, the solvent is Cu, but in Ni–Cu, the solvent is Ni.

alloys, and in Fig. 4 the thermal-expansion data of some of these are compared with our theoretical curves.[5] Here again, agreement is usually within experimental error. It is interesting that if a weighted average of Ni in Cu and Cu in Ni is used in calculating the theoretical thermal expansion of the commercial Cu, 45 at.% Ni alloy, agreement is still within 2% of the observed thermal expansion; i.e., 14.6 deg C^{-1} compared with 14.9 deg C^{-1}.

While the theory can be satisfactorily applied to solid-solution alloys in which no solid-state transformations occur, we do not expect our simple approach to predict the thermal expansion of alloys in which magnetic and order-disorder transformations occur. The failure of the theory in the latter case is borne out by the divergence between theory and the dilatometric data for Fe-Al alloys by McQueen and Kuczynski.[6] A similar failure of the theory occurred with the low thermal-expansion Fe-Ni alloys in which magnetic and phase transformations combine to cause abnormal expansion behavior.[5]

Values of the elastic constants E and ν and the constants A and V_d of our equation are listed in Tables I and II for the alloy systems considered in this study.

TABLE I. Elastic constants of various metals.[a]

Element	Young's modulus	Poisson's ratio
Cu	17.0×10^6 psi	0.33
Zn	14.8×10^6 psi	0.25
Ni	29.0×10^6 psi	0.29
Au	11.1×10^6 psi	0.42
Al	9.0×10^6 psi	0.25
Fe	28.5×10^6 psi	0.29
Mg	6.3×10^6 psi	0.25
Cr	36.0×10^6 psi	0.29

[a] When the elastic constants had a range of values, the value which gave the best theoretical agreement was used.

CONCLUSION

The thermal expansion equation derived from an elastic continuum model for solid-solution binary alloys is largely substantiated by experimental results for alloys in which no complications arise, such as order-disorder and magnetic transformations. For these alloys, agreement is often within experimental error, and is best for dilute alloys in which the constituents have the same crystal structure as the alloy. These limitations are in complete agreement with the limitations imposed by the model assumed.

Agreement is best over the temperature ranges for which the experimental data for the pure constituents and the alloys exhibit Grueneisen behavior. This eliminates temperature ranges of order-disorder and magnetic transformations in the alloy, and polymorphic and magnetic transformations in the pure constituents. The thermal-expansion equation cannot be used at temperatures near or above the melting point of the lowest melting constituent since here the constants of the equation are either unknown or do not exist.

ACKNOWLEDGMENTS

We would like to express our gratitude to Dr. Toshio Mura for his assistance in the development of our thermal-expansion equations.

---

[6] H. J. McQueen and G. C. Kuczynski, Trans. AIME **215**, 619 (1959).