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The Thermal Expansion of Anisotropic Metals

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A review of the present state of knowledge of the variation with temperature of the thermal expansion of anisotropic metals. The theoretical significance of the experimental data is discussed.

INTRODUCTION

The thermal expansion of a noncubic crystal can be specified completely in terms of the linear expansion coefficients, $\alpha_x\ \alpha_y\ \alpha_z$, measured along three mutually perpendicular axes. These axes, in the case of the rhombic and tetragonal systems, correspond with the crystallographic axes. In the hexagonal and rhombohedral systems the axis of highest rotational symmetry coincides with one of the expansion axes; the direction of the second expansion axis is chosen arbitrarily. In the monoclinic system one of the expansion axes coincides with the b axis of the crystal and the direction of one of the other two expansion axes depends upon the particular crystal under consideration, while in the triclinic system there is, in general, no relation between the crystal and expansion axes.

The thermal expansion coefficient α_{lmn}, in the direction having direction cosines l, m, n with the coordinate axes, is given by

$$\alpha_{lmn}=\alpha_x l^2+\alpha_y m^2+\alpha_z n^2,$$

which, for the three uniaxial systems that comprise the majority of anisotropic metals, reduces to

$$\alpha_\theta=\alpha_{\parallel}\cos^2\theta+\alpha_{\perp}\sin^2\theta,$$

where θ is the angle between the given direction and the principal axis, and $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the expansion coefficients in the directions parallel and perpendicular to the principal axis.

A complete specification of the expansion of such a crystal requires a knowledge of the two, or three, expansion coefficients as functions of temperature over the whole range from the absolute zero to the melting point. In the past, relatively little attention has been paid to the study of the expansion of anisotropic metals, and for only 10 out of the 34 metals that have anisotropic structures have values for the expansion coefficients been obtained at more than one temperature. Some of these values must, in addition, be regarded as uncertain. Even less information is available for anisotropic alloys.

In view of the practical and fundamental importance of the subject the lack of interest in the expansion of anisotropic substances is remarkable. For example, much information with regard to the directional dependence of the binding forces and lattice vibrations in anisotropic metals can be obtained from a study of the expansion of such bodies. In order to stimulate interest, therefore, experimental data for the expansion of anisotropic metals are summarized in this paper, and a brief account of the theoretical relations that have been derived for the observed behavior is given.

I. HUME-ROTHERY'S CLASSIFICATION

In dealing with the experimental results it is convenient to adopt Hume-Rothery's classification (1)* in which the elements in the periodic table are separated (by continuous lines) into four classes (see Fig. 1). Class I, at the extreme left of the table, comprises those metals that crystallize in the three typically metallic structures, the face- and body-centered cubic systems and the hexagonal close-packed system with an axial ratio of 1.63. In these structures each atom has 8 or 12 equidistant neighbors so that, to a first approximation, the force field acting on the atom may be considered as spherically symmetrical. Consequently, these metals show relatively slight anisotropy in their elastic and thermal properties.

Elements in Class III include metals and semimetals with a valency of four or more. These tend to form structures in which the atoms are bound by covalent forces into clusters of $(8-N)$ atoms, where N is the valency. The binding forces between clusters are weaker than those within the clusters, and consequently, considerable anisotropy results. Thus, the atoms in selenium and tellurium with 6 electrons in their outer shells form into spiral chains, each atom having two nearest neighbors. The expansion in the direction of the chains is markedly different from that in the direction perpendicular to the chains.

Class II includes metals with structures intermediate between those of Class I and III. Thus zinc and cadmium possess structures which, though hexagonal close-packed, have axial ratios of 1.86 and 1.89, respectively, instead of 1.63.

Class IV consists of nonmetals and is therefore not of interest here.

II. CLASS I METALS

For thermal expansion, as also for many other properties, magnesium (Fig. 2) is virtually isotropic—more so, in fact, than iron. At room temperature, where the coefficients differ to the greatest extent, $\alpha_{\perp}$ is 95 per-

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* Numbers in parentheses refer to Bibliography at end of paper.

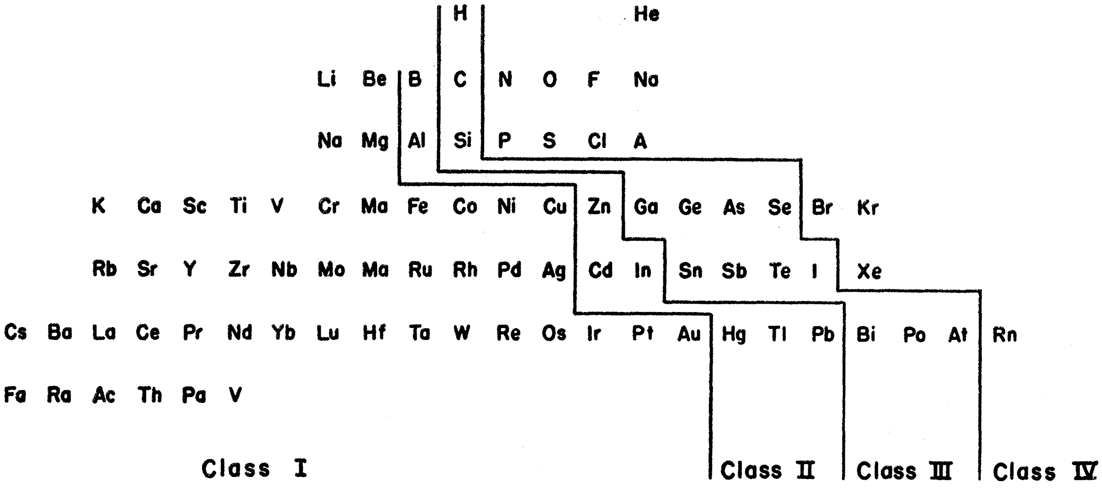

FIG. 1. Hume-Rothery's classification of the elements.

cent of $\alpha_{\parallel}$. Both $\alpha_{\perp}$ and $\alpha_{\parallel}$ increase monotonically with temperature, the increase being particularly marked between 0 and 300°K and above 600°K. This kind of variation is found also for several other metals. The chief feature of interest in magnesium, however, is the excellent agreement between the values obtained by Hume-Rothery and Raynor (5) who measured the expansion of the magnesium lattice by an x-ray diffraction method, and those obtained by Goens and Schmid (3) who used a Henning comparator to measure the expansion of bulk single crystals of various orientations. This agreement between values obtained by these two essentially different methods, though of general occurrence, is not necessarily to be expected. It depends, on the one hand, upon the degree of perfection of the bulk crystals and the extent to which they deform plastically when loaded, and, on the other hand, upon the amount of strain which is present, because of the anisotropy, in the polycrystalline specimens used in the x-ray measurements. The other results for magnesium appear to be somewhat less accurate, but even so, there is no systematic disagreement between the crystal measurements of Bridgman (2) and the lattice measurements of the other investigators.

Beryllium (Fig. 3) is also relatively isotropic, though less so than magnesium. There is some discrepancy between the results of Gordon (7) and those of Owen and Richards (9), though both used x-ray methods. This discrepancy is particularly marked at the lower temperatures, where Gordon finds a steep fall, below about 420°K, in the values of the coefficients. Because of the high Debye temperature (1000°K) of beryllium such a fall may be expected so that it is likely that Gordon's results are the more reliable. The bulk crystal values for the expansion coefficients of beryllium obtained by Bridgman (2) and by Treco (10) do not deviate systematically from the lattice expansion values obtained by the other investigators.

In Table I expansion data for osmium, ruthenium, α-cobalt, zirconium, rhenium, and α uranium are given. Osmium and ruthenium, as expected from their strong binding forces and consequently high melting points and low compressibilities, have small expansion coefficients. These depend only slightly on temperature and do not differ greatly. Zirconium, rhenium, and α uranium are exceptions to the Hume-Rothery classification. They are all strongly anisotropic in their thermal expansion. Uranium has a complex orthorhombic structure below 650°C, and one of its expansion coefficients is negative.

III. CLASS II METALS

The expansion coefficients of all the five anisotropic metals in Class II have been measured. In Fig. 4 $\alpha_{\perp}$ for zinc is shown. Except for the inaccurate results of Austin (13), there is good agreement, particularly between the lattice expansion measurements of Owen and Yates (16) and the bulk crystal data of Grüneisen and Goens (15). The general dependence of $\alpha_{\perp}$ on temperature is similar to that for magnesium, except that $\alpha_{\perp}$ becomes negative at about 70°K.

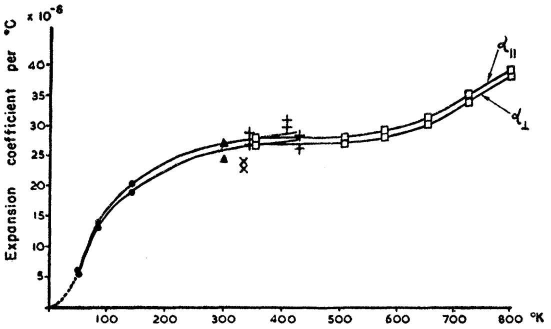

FIG. 2. $\alpha_{\parallel}$ and $\alpha_{\perp}$ for magnesium. ▲ Bridgman (2). ● Goens and Schmid (3). + Hannawalt and Frevel (4). □ Hume-Rothery and Raynor (5). × Shinoda (6).

For $\alpha_{\parallel}$, however, there is not such good agreement (Fig. 5). In the overlapping region the results of Owen and Yates (16) are lower than those of Grüneisen and Goens (15) and are probably less accurate. The remarkable feature is the rapid rise of $\alpha_{\parallel}$ to a large maximum value at 120°K followed by a progressive fall to the melting point.

Cadmium (Fig. 6), as expected from its similar crystal structure and axial ratio, behaves similarly to zinc; $\alpha_{\parallel}$ has a high maximum value, and $\alpha_{\perp}$ a negative value at low temperatures. An additional feature of interest is that at 523°K cadmium becomes isotropic in expansion.

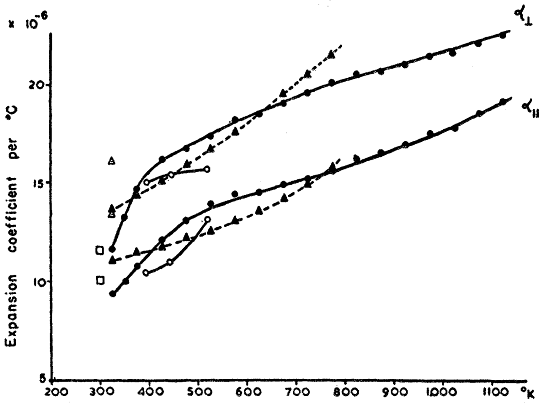

FIG. 3. $\alpha_{\parallel}$ and $\alpha_{\perp}$ for beryllium. △ Bridgman (2). ● Gordon (7). ○ Kossolapow and Trapesnikow (8). ▲ Owen and Richards (9). □ Treco (10).

Mercury (Fig. 7), unlike zinc and cadmium, is only feebly anisotropic in expansion. This is remarkable since its linear compressibilities are in the ratio 1:5 and, more especially, since the direction of greatest expansion corresponds to the direction of smallest compressibility or strongest binding.

TABLE I. Expansion coefficients of some metals in Class I.

Metal	Structure	$10^6\alpha_{\parallel}$ per °C	$10^6\alpha_{\perp}$ per °C	Temp. °C	Reference
Os (c.p.)	hexagonal	5.9– 8.35	4.0–5.85	50–550	9
Ru (c.p.)	hexagonal	8.8–11.7	5.9–7.65	50–550	9
α-Co (c.p.)	hexagonal	16.1	12.6	60	6
Zr (c.p.)	hexagonal	2.5	14.3	80	6
Re (c.p.)	hexagonal	12.5	4.7	20	11
		$10^6\alpha_a$	$10^6\alpha_b$	$10^6\alpha_c$		
α-U	orthorhombic	23	−3.5	17	150	12

For thallium and indium, which have hexagonal close-packed and tetragonal structures, respectively, only single mean values of the expansion coefficients are available. These are for thallium at 60°C, $\alpha_{\parallel}=72\times10^{-6}$, $\alpha_{\perp}=9\times10^{-6}$, and for indium at 50°C, $\alpha_{\parallel}=11.7\times10^{-6}$, $\alpha_{\perp}=45.0\times10^{-6}$ in deg^{-1}C. Both metals are thus highly anisotropic.

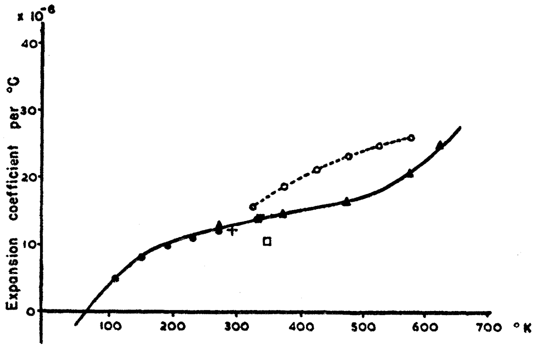

FIG. 4. $\alpha_{\perp}$ for zinc. ○ Austin (13). + Bridgman (14). ● Grüneisen and Goens (15). ▲ Owen and Yates (16). □ Shinoda (17). ▼ Staker (18).

IV. CLASS III METALS

In Class III only tin and bismuth have been investigated thoroughly. Using an interferometric method and bulk crystals, Childs and Weintroub (23) found that for tin $\alpha_{\parallel}$ was approximately twice $\alpha_{\perp}$ and that both coefficients increased almost linearly with temperature from room temperature to the melting point (see Fig. 8). The single values obtained by the other in-

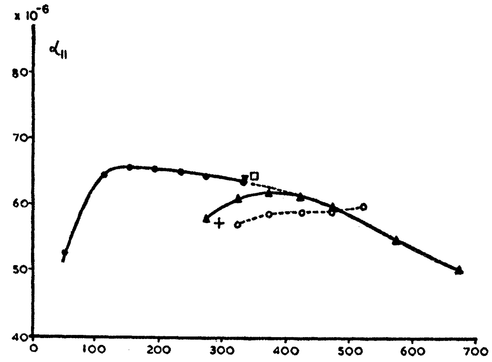

FIG. 5. $\alpha_{\parallel}$ for zinc. ○ Austin (13). + Bridgman (14). ● Grüneisen and Goens (15). ▲ Owen and Yates (16). □ Shinoda (17). ▼ Staker (18).

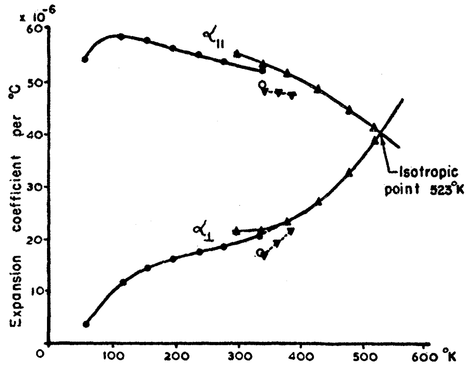

FIG. 6. $\alpha_{\parallel}$ and $\alpha_{\perp}$ for cadmium. ● Grüneisen and Goens (15). ▼ Kossolapow and Trapesnikow (19). ▲ Owen and Roberts (20). ○ Shinoda (6).

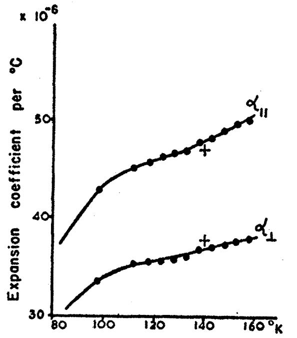

FIG. 7. $\alpha_{\parallel}$ and $\alpha_{\perp}$ for mercury. + Grüneisen and and Sckell (21). ● Hill (22).

vestigators differ considerably from those of Childs and Weintroub; two lattice expansion values lie above the curves, and one bulk crystal result lies below. This separation between the lattice and crystal results may not be significant, however, in view of the disagreement between the individual values in the two groups.

Bismuth, antimony, and arsenic have a rhombohedral structure in which the atoms are arranged in double layers perpendicular to the principal expansion axis. Because of the many anomalies in its physical properties bismuth has been the subject of detailed investigation. The remarkable constancy of the coefficients $\alpha_{\parallel}$ and $\alpha_{\perp}$, which for $\alpha_{\parallel}$ extends over a range of 360°K, should be noted (see Fig. 9). Another feature of interest is the discontinuous changes at 258 and 345°K which have been observed by two investigators. These discontinuities cannot be interpreted as due to a phase change since no similar discontinuities have been observed in the variation of the lattice constants with temperature. Finally, the fall in $\alpha_{\parallel}$ and $\alpha_{\perp}$ which begins near the melting point and which has been found by Buchta and Goetz (29) to be due to the presence of small amounts of impurity should be noted.

The relatively looser structure of antimony perpendicular to the layers makes antimony more anisotropic than bismuth. The coefficients (Fig. 10), similar to those for bismuth, do not appear to vary appreciably with temperature, but this is not established definitely since the measurements are fewer and less accurate.

Arsenic (Table II), being relatively less strongly bound perpendicular to the layers even than antimony, is still more anisotropic. No information about the temperature dependence of the coefficients is available.

Hexagonal selenium and tellurium are the most anisotropic substances so far investigated. $\alpha_{\parallel}$ for selenium is very negative even at room temperatures, while $\alpha_{\perp}$ has a large positive value. This is in consequence of the strong covalent binding parallel to the chains, coupled with weak molecular type forces which hold the chains together. Similarly, graphite, with an hexagonal layer structure, has a relatively large $\alpha_{\parallel}$ in the direction of weak molecular binding and a negative $\alpha_{\perp}$ in the direction of the strong covalent forces.

V. THEORY AND DISCUSSION

A physical explanation of the thermal expansion of substances may be given by considering Fig. 11 in which the potential energy E of a pair of atoms is plotted as a function of their distance d apart. The important feature of this curve is the lack of symmetry about the minimum at the equilibrium distance d_0. Thus the displacement from the equilibrium position required to produce a given change in potential energy is greater for an increase than for a decrease in d. Hence, if the atoms vibrate longitudinally, corresponding to the lattice vibrations of a solid, a net outward pressure will be set up which will produce an expansion, Δd, in the mean interatomic distance. This will increase as the amplitude of vibration increases with rise in temperature. If the vibrational energy is quantized, then for temperatures much greater than the characteristic temperature, a linear relationship between Δd and E results in a constant expansion coefficient α, while at temperatures less than the characteristic temperature where E is no longer proportional to the temperature, α falls progressively. This simple argument can be extended to two and three dimensions and, if certain assumptions are made concerning the shape of the potential curve, leads to the well-known Grüneisen's law relating the thermal expansion and the specific heat of isotropic substances.

For anisotropic substances the general situation is very similar, but for these the dependence of the potential energy curve, and consequently of the linear compressibilities on direction, has two important consequences. The first is that at low temperatures lattice vibrations will be excited preferentially in the direction of greatest compressibility on account of the lower vibrational frequencies. Thus, initially, the expansion parallel to this direction will be greater than in the perpendicular direction. The second is that an expansion in one direction is accompanied by an elastic contraction in the perpendicular directions, the magnitude of which is determined by the magnitude of the expansion and, for the principal directions, by the elastic coefficients s_{12}, s_{13}, s_{23}. This contraction may be sufficiently

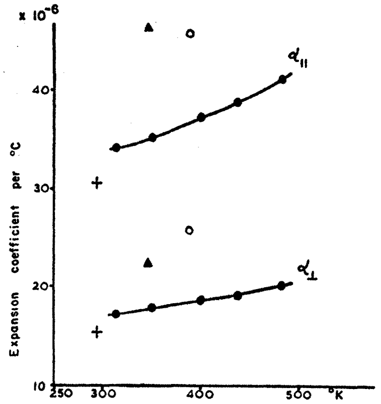

FIG. 8. $\alpha_{\parallel}$ and $\alpha_{\perp}$ for tin. + Bridgman (14). ● Childs and Weintroub (23). ▲ Kossolapow and Trapesnikow (8). ○ Shinoda (17).

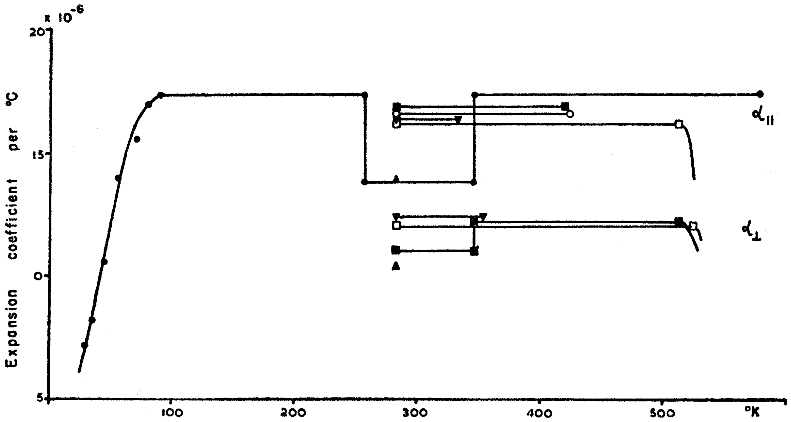

FIG. 9. $\alpha_{\parallel}$ and $\alpha_{\perp}$ for bismuth. ▲ Bridgman (14). ▼ Fizeau (24). ● Jacobs and Goetz (25). ■ Jay (26). ○ Ho and Goetz (27). □ Roberts (28).

great to overcome the intrinsically small expansion in these directions at low temperatures and produce a net contraction. This occurs for zinc, cadmium, graphite, selenium, tellurium, and uranium, and probably also for thallium, indium, and arsenic.

This qualitative treatment has been applied by Grüneisen and Goens (15) to anisotropic (hexagonal) crystals and by making several simplifying assumptions they have derived theoretical relationships for $\alpha_{\parallel}$ and $\alpha_{\perp}$. They have used these to interpret their experimental results for zinc and cadmium at low temperatures. Commencing with the thermodynamical relations, if X_x and Z_z are the "thermal pressures,"

$$\alpha_{\perp}=\alpha_x=\alpha_y=\frac{1}{l_x}\left(\frac{\partial l_x}{\partial T}\right)_p=\frac{1}{V}\int_0^T\left(\frac{\partial C_p}{\partial X_x}\right)\frac{dT}{T},$$

$$\alpha_{\parallel}=\alpha_z=\frac{1}{l_z}\left(\frac{\partial l_z}{\partial T}\right)_p=\frac{1}{V}\int_0^T\left(\frac{\partial C_p}{\partial Z_z}\right)\frac{dT}{T},$$

where V is the volume and C_p the specific heat at constant pressure; C_p is replaced by C_v, the specific heat at constant volume, and the Born (35) expression for C_v is substituted. This expression takes account of the variation of the limiting frequencies, i.e., the characteristic temperatures Θ^i, with the nature and direction of the lattice vibrations. Grüneisen and Goens (15) obtained

$$\alpha_x=(s_{11}+s_{12})q_x+s_{13}q_z,$$

$$\alpha_z=2s_{13}q_x+s_{33}q_z,$$

TABLE II. Expansion coefficients of some metals in Class III.

Metal	Structure	$10^6\alpha_{\parallel}$ per °C	$10^6\alpha_{\perp}$ per °C	Temp. °C	Reference
As	rhombohedral	43	3	6	31
C	hexagonal	27.6–29.0	−1.5–0.9	85–750	32
Te	hexagonal	−1.7	27.5	45	33
		−1.6	27.2	25	14
Se	hexagonal	−17.9	74.1	45	33
		$10^6\alpha_a$ $10^6\alpha_b$	$10^6\alpha_c$ $10^6\alpha_\beta$		
Se	monoclinic	−1.5 84.7	63.3 5.5	20	34

where

$$q_x=\frac{R}{V}\sum_{j=1}^{3}\int\gamma_x{}^jD\left(\frac{\Theta_x{}^j}{T}\right)\frac{d\Omega}{4\pi}$$

and

$$q_z=\frac{R}{V}\sum_{j=1}^{3}\int\gamma_z{}^jD\left(\frac{\Theta^j}{T}\right)\frac{d\Omega}{4\pi}$$

are the so-called "thermal pressure coefficients," D is the Debye function, $\gamma_x{}^j=(\partial\log\Theta_x{}^j/\partial\log l_x)$, etc., and $j=1, 2, 3$ refers to the acoustical modes of vibration. Finally as in the Debye theory of specific heats the distinction between the Θ^j's and the γ^j's is removed and mean values (indicated by $\langle\,\rangle$) substituted so that

$$\alpha_x=\frac{3R}{V}\left[(s_{11}+s_{12})\langle\gamma_x\rangle D\left(\frac{\langle\Theta_x\rangle}{T}\right)+s_{13}\langle\gamma_z\rangle D\left(\frac{\langle\Theta_z\rangle}{T}\right)\right],$$

$$\alpha_z=\frac{3R}{V}\left[2s_{13}\langle\gamma_x\rangle D\left(\frac{\langle\Theta_x\rangle}{T}\right)+s_{33}\langle\gamma_z\rangle D\left(\frac{\langle\Theta_z\rangle}{T}\right)\right].$$

The values of $\langle\gamma\rangle$ and $\langle\Theta\rangle$ have to be chosen empirically to give agreement between the theoretical and experimental values of α.

In Fig. 12 the agreement which can be obtained with

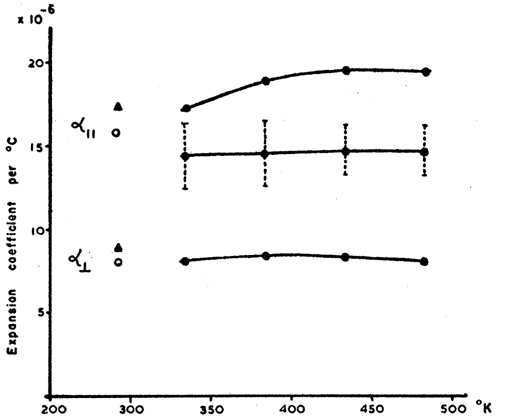

FIG. 10. $\alpha_{\parallel}$ and $\alpha_{\perp}$ for antimony. ○ Bridgman (14). ▲ Fizeau (24). ● Hidnert (30).

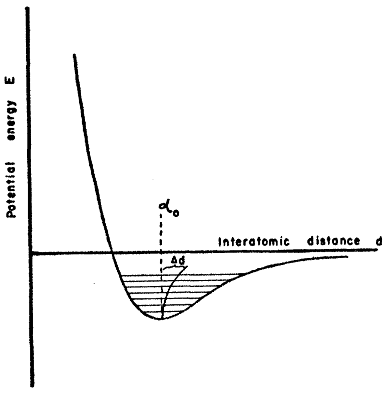

FIG. 11. The variation of potential energy with distance.

experiment is illustrated for the case of zinc. The values used by Grüneisen and Goens were $\langle\gamma_x\rangle = 2.04$, $\langle\gamma_z\rangle = 1.68$ which are of the same order as those for isotropic substances, and $\langle\Theta_x\rangle = 320°\text{K}$, $\langle\Theta_z\rangle = 200°\text{K}$, compared with $\Theta = 250°\text{K}$ from specific heat measurements. The agreement, however, is not a true measure of the correctness of the formulas, because the various approximations and simplifications are obscured by the choice of the values for the $\langle\gamma\rangle$'s and $\langle\Theta\rangle$'s. For example, the elastic coefficients are assumed to be independent of temperature. It must be remembered also that the assumptions involved in the Debye theory regarding the frequency spectrum of the lattice vibrations, introduced errors at low temperatures, and the assumption of the equality of C_p and C_v introduces error at high temperatures. (For a modification of the Grüneisen-Goens theory applicable at high temperatures see Riley (36).)

CONCLUSION

It should be clear from the above summary both of the experimental data and of the theoretical formulas for the expansion of anisotropic metals that it is desirable that much additional information be obtained, by accurate measurement, of the linear expansion coefficients over wide ranges of temperature and, by calculation from the elastic coefficients, of the spatial variation of the γ's and Θ's.

ACKNOWLEDGMENTS

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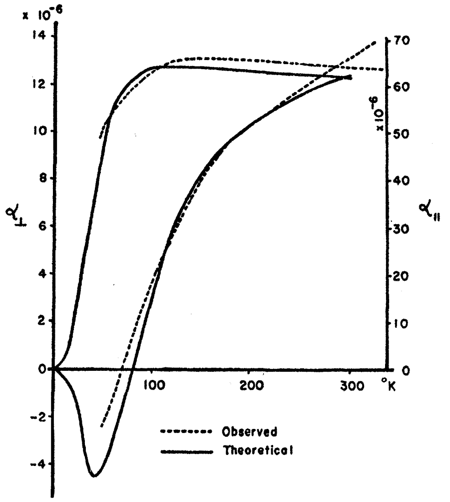

FIG. 12. Theoretical and observed values of $\alpha_\parallel$ and $\alpha_\perp$ for zinc, after Grüneisen and Goens (reference 15).

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