Short Communications

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A useful relationship between atomic vibration amplitudes and thermal expansion for cubic solids.

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Grüneisen (1926) has derived a simple and useful relationship between the mean square atomic vibration amplitude and the thermal expansion for cubic solids.

$$\langle u^2\rangle_{Av} = \frac{3r_0^2}{8\pi^2\gamma Z^2} \cdot \frac{\Delta V}{V_0}, \qquad (1)^*$$

where $\langle u^2\rangle_{Av}$ = mean square thermal atomic vibration amplitude,

r_0^3 = atomic volume,

$\Delta V/V_0$ = fractional increase in volume relative to absolute zero,

γ = Grüneisen constant,

Z^2 = constant for a given material, calculated from a central force model (Grüneisen, 1926).

At the time equation (1) was first developed, there were insufficient precision data to confirm this relationship. However, in the past few years sufficient mean square amplitude data have become available in the literature to warrant a critical examination of this relationship. All of the necessary experimental information is obtainable from X-ray diffraction data. It is the purpose of this communication to demonstrate the validity of equation (1) over a wide range of temperature using X-ray diffraction data collected from a variety of cubic materials.

For a powder pattern, the decrease in diffracted X-ray integrated intensity with increasing temperature is given by

$$I = AjF^2(\mathrm{Lp}) \exp(-2M), \qquad (2)$$

where A is a constant, j is the multiplicity, F is the structure factor, (Lp) is the Lorentz-polarization factor,

$$M = \tfrac{8}{3}\pi^2\langle u^2\rangle_{Av}\frac{\sin^2\theta}{\lambda^2},$$

θ is the Bragg angle, and λ is the X-ray wavelength. The mean square amplitude can be related to the Debye temperature using

$$\langle u^2\rangle_{Av} = \frac{9h^2T[\varphi(x)+x/4]}{4\pi^2\bar{m}k\Theta^2}, \qquad (3)$$

where h is Planck's constant, k is the Boltzmann constant, T is the temperature, Θ the Debye temperature, $\bar{m}$ the mean atomic mass, $x = \Theta/T$ and $\varphi(x)$ is the Debye integral.

* For a simplified treatment see Stein (1964).

Experimental values of Θ as a function of temperature are available for Al, Cu, Au (Owen, 1947), Pb (Chipman, 1960), Ag (Simerska, 1961), Fe (Gazzara, 1960), W, TiC, ZrC, TiN and ZrN (Houska, 1964). Mean square amplitudes calculated by equation (3) are displayed in Fig. 1. Linear thermal expansion data are available for W, TiC, ZrC, TiN and ZrN (Houska, 1964); for Al, Ag, Au, Fe and Cu (Goldsmith, Waterman & Hirschhorn, 1961); and for Pb (Hindert & Sweeney, 1932). All of these thermal expansion data are displayed in Fig. 2.

For convenience, equation (1) is written in terms of linear expansion relative to absolute zero:

$$\langle u^2\rangle_{Av} = \frac{9r_0^2}{8\pi^2\gamma Z^2} \cdot \frac{a(T)-a_0}{a_0}, \qquad (4)$$

and, from the foregoing results, we obtain the final curves given in Fig. 3. An examination of these results clearly indicates that all of the curves, except those for lead and silver at the lowest and highest temperatures, are straight lines. It is evident that the product γZ^2 can be treated as a constant for a given cubic material and that equation (4) provides a good representation of the data. A further examination of these curves indicates that all have approximately the same slope (lead is again the exception), and therefore nearly the same values of γZ^2. Table 1 gives a listing of γZ^2 along with γ (Grüneisen, 1926) and Z^2. Although both γ and Z^2 take on a range of values when considered separately, the product is seen to be nearly constant with an average value of 0·145 (lead is again excluded). It can be concluded, from the available data, that equation (4) appears to give a good approximation for $\langle u^2\rangle_{Av}$ if γZ^2 is taken equal to 0·145. This, of course, is restricted to cubic materials and further generalizations cannot be made without additional data.

Table 1. *Calculated values of the factor* Z^2 *from the curves of Fig.* 3

Material	Lattice parameter	r^2	γZ^2	γ	Z^2
Aluminum (f.c.c.)	4·049 Å	6·50 Å^2	0·1468	2·17	0·0675
Copper (f.c.c.)	3·614	5·18	0·1322	1·96	0·0675
Iron (b.c.c.)	2·866	5·17	0·1495	1·60	0·0935
Gold (f.c.c.)	4·078	6·60	0·1316	3·03	0·0434
Lead (f.c.c.)	4·941	9·40	0·0676	2·37	0·0248

Table 1 (*cont.*)

Material	Lattice parameter	r^2	γZ^2	γ	Z^2
Silver (f.c.c.)	4·078	6·60	0·1376	2·40	0·0574
Tungsten (b.c.c.)	3·165	6·32	0·1640	1·62	0·1012
Titanium carbide (NaCl)	4·326	4·69	0·1510	*	
Titanium nitride (NaCl)	4·242	4·50	0·1379	*	
Zirconium carbide (NaCl)	4·696	5·51	0·1510	*	
Zirconium nitride (NaCl)	4·575	5·28	0·1638	*	

It should be noted that the experimental values of Z^2 depend upon the definition of r_0. If another definition is used, Z^2 values will be modified by a constant factor.

* These values not available.

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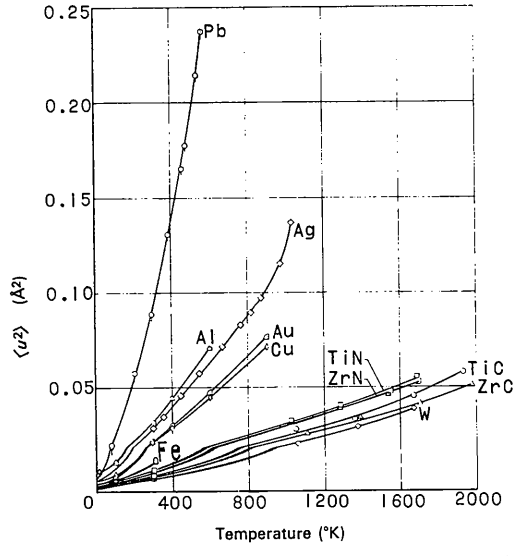

Fig. 1. Variation of mean square vibrational amplitude with temperature for several metals and compounds.

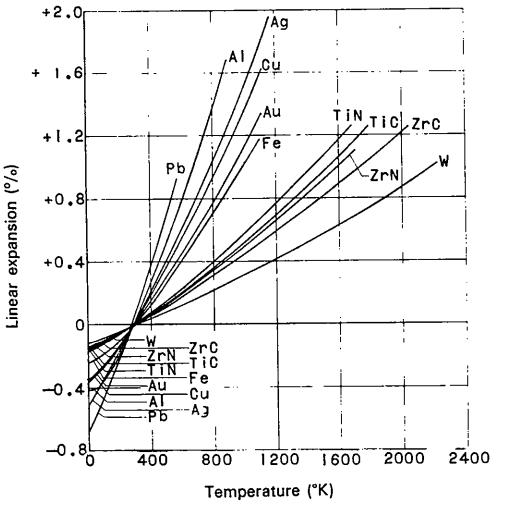

Fig. 2. Variation of linear thermal expansion with temperature for several metals and compounds. All changes are relative to 25°C.

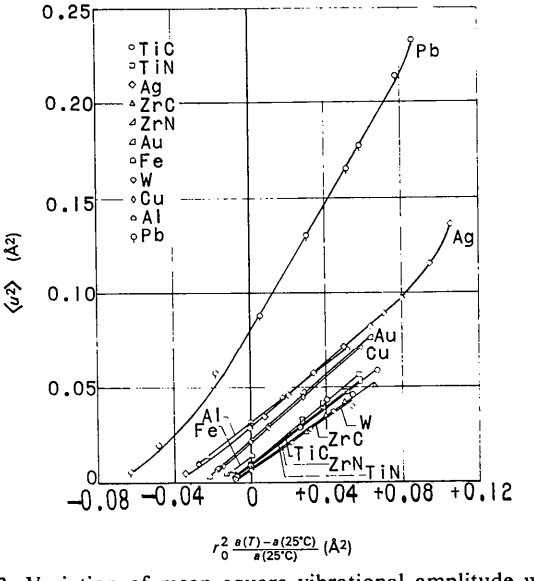

Fig. 3. Variation of mean square vibrational amplitude with the product of linear thermal expansion and r_0^2 for several metals and compounds.