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58 60 62 64 66 68 70 La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Atomic number

FIG. 33. (a) Grüncisen constant, γ_{θ} , as calculated from C_v , of the rare-earth metals. (b) Size factor of the rare-earth metals. Open points are estimated data.

poor (Be, C(g), Si, Mn, Co, Ge, Rb, Zr, Ru, Pd, Ag, La, Ce(γ), Lu, Ta, W, Ir, Pt, Bi, and U). Of the elements which are included in the "poor" category, the compressibility data for 8 of the metals (Ru, Pd, Ag, γ -Ce, W, Ir, Pt, and U) was suspected of being incorrect (see Section 24). The compressibility data of Mn and Rb had been questioned by Gilvarry,¹⁰⁷ and this may explain the poor agreement for these two elements. If these elements are excluded from the above analysis, then we would have 18 very good, 11 good, 11 fair, and 10 poor. Thus it would appear that one finds reasonable agreement between γ_G and γ_S , as had been proposed by Slater.

The mean value for γ_s was found to be 1.64 ± 0.91 , if the value for the elements Ru, Ag, γ -Ce, Pd, and W are excluded from the average. The error ± 0.91 corresponds to the percentage error of ± 55.5 , which is slightly poorer than that for γ_G .

PHYSICAL PROPERTIES AND INTERRELATIONSHIPS

Grüneisen Constant γ_{SW} . The Grüneisen constant as determined from shock wave data, γ_{SW} , was also compared with γ_G . It was found that γ_{SW} was smaller than γ_G for 17 elements and greater for 9 elements (almost 2 to 1). By using the same criteria as given above, it was found that very good agreement was obtained for 22 elements (Be, Na, Mg, Ti, V, Co, Ni, Cu, Zn, Zr, Nb, Mo, Rh, Pd, Ag, Cd In, Sn(w), W, Tl, Pb, and Th); good agreement for 3 elements (Cr, Pt, and Au); and poor agreement only for tantalum. This indicates that $\gamma_G = \gamma_{SW}$ is a very good approximation.

Since the agreement between γ_G and γ_{SW} is good for Be, Co, and Zr (3 of the 10 remaining elements for which γ_S is in poor agreement with γ_G), this places a higher degree of confidence on γ_G for these 3 elements and therefore suggests that γ_S may be unreliable because of inaccuracy in the compressibility data, especially in the *b* (pressure-dependence) term.

It is interesting to find that $\gamma_{SW} \simeq \gamma_S$ for tantalum and that both of these values are very much smaller than γ_{σ} . Perhaps the value for γ_{σ} is incorrect, although this seems unlikely since the values of α , V, χ , and C_* are reasonably well established.

The mean value for γ_{SW} is 1.76, which is somewhat larger than the mean value of γ_G , 1.57. Since it was mentioned above that γ_{SW} is usually smaller than γ_G , the reverse relationship between the means is somewhat surprising. However, if one takes the average for the same elements for which γ_G , γ_S , and γ_{SW} are all known (Be, Mg, Al, Ti, V, Cr, Co, Ni, Cu, Zn, Zr, Nb, Mo, Rh, Cd, In, Sn(w), Ta, Pt, Au, Tl, Pb, and Th), we find the mean values to be 1.98, 1.67, and 1.76, respectively.

Gschneidner and Vineyard⁴ have used the Grüneisen constant to predict departures from Vegard's law (which states that the lattice constants of binary alloys vary linearly between the two end-menbers). They found that their method, based on second-order elasticity, described the sign and order of magnitude of departures from Vegard's law in binary alloy systems better than did previous techniques given in the literature.

Estimated Data. In calculating γ_G from C_*^l and C_* , there are a few elements for which the coefficient of expansion, the compressibility, or the heat capacity at constant volume (C_*^l and C_*) were not known experimentally. If any one of these quantities was estimated, then γ_G was considered to be estimated also.

29. Size Factor

Eshelby's Approach. Eshelby¹¹⁸ has pointed out in his review paper on the continuum theory of lattice defects that it is possible to derive

118 J. D. Eshelby, Solid State Phys. 3, 79 (1956).

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