HIGH PRESSURE MÖSSBAUER STUDIES

can calculate the one atmosphere value from

$$\theta_0 = \left(\frac{V_p}{V_0}\right)^{\nu} \theta_p \tag{27}$$

where γ is the Grüneisen constant.

The resultant values for θ are listed in Table I. Since the f number measures a mean value of $\langle \omega^{-2} \rangle$ where ω is the lattice vibrational

TABLE I. Mössbauer and Grüneisen constants for copper, vanadium and titanium

Element	50 kb		Atmospheric		
	$\theta_f(^{\circ}\mathrm{K})$	$\theta_{\rm host}(^{\circ}{\rm K})$	$\theta_f(^{\circ}\mathrm{K})$	$\theta_{\rm host}(^{\circ}{\rm K})$	Y
Cu	350 ± 14	331 ± 14	327 ± 14	309 ± 14	1.998
v	268 ± 10	284 ± 11	258 ± 10	274 ± 11	1.257
Ti	339 ± 35	370 ± 40	321 ± 35	350 ± 40	$1 \cdot 232$

frequency, it is most meaningful to compare these θ 's with θ obtained from X-ray diffraction measurements. Unfortunately, this can only be done for copper. Table II summarizes the available data for this metal. It can be seen that the X-ray results are in excellent agreement with the predictions from high pressure Mössbauer data.

TABLE II. θ_D from X-ray measurements for copper

Investigators	Debye parameter (°K)		
Owen and Williams (1947)	314		
Burie (1956)	299		
Chipman and Paskin (1959)	307 (327) ^a		
Flinn et al. (1961)	322		
Graevskaya et al. (1965)	310		

* Parenthetic value corrected for one and two phonon generation.

A direct comparison of these results with other data for vanadium is more difficult. The values of θ available are from low temperature specific heat measurements and are listed in Table III. It should be kept in mind that vanadium is superconducting below 5.4°K so that measurements must be made in a field 5–10 kgauss. Further, a large correction for electronic specific heat is necessary. The results in Table IV show a rather distinct trend with sample purity, with the more impure samples agreeing with our result. This is perhaps

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TABLE III. θ_D from specific heat measurements for vanadium

Sample purity (%) γ_{C} (°K)			
	>99.98	380	
sample 1:	99.50	308	
sample 2:	99.80	273	
	≈99·80	338	
	99.50	425 ^a	
	>99.99	382	
	Sample pu sample 1: sample 2:	Sample purity (%) >99.98 sample 1: 99.50 sample 2: 99.80 ≃99.50 >99.99	Sample purity (%) $\gamma \sigma$ (°K) > 99.98 380 sample 1: 99.50 308 sample 2: 99.80 273 $\simeq 99.80$ 338 99.50 425 ^a > 99.99 382

* Experiment performed in temperature range 11-23°K.

reasonable, as our samples contained ⁵⁷Co (⁵⁷Fe) impurity. It must be remembered that θ_{C_p} is a distinct function of temperature and may be 50° or more lower at room temperature.

For titanium, Wolcott (1957) and Johnson and Kothen (1953) have made C_v measurements over a long temperature range. At low temperatures they obtain $\theta = 430$ °K and near room temperature a value of 360 °K, in very good agreement with these results.

The results for these three metals demonstrate that, to a good approximation, γ is independent of density at least to 100 kb, which validates the Grüneisen equation of state over this range and permits the prediction of θ as a function of pressure to 100 kb at least.

TABLE IV. Constants A and B for relationship $K = AP_B$

Compound	A	В
FeCl ₃	0.265	0.56
FeBr ₃	0.076	0.43
KFeCl4	0.092	0.50
FePO ₄	0.078	0.46
Phosphate Glass	0.048	0.31
Ferric Acetate (418°K)	0.022	0.98
Ferric Citrate	0.112	0.35
K ₃ Fe(CN) ₆	0.109	2.06

E. CONVERSION OF FeIII TO FeII

As has been emphasized in the earlier sections, the Mössbauer spectra of high spin ferrous and high spin ferric iron are entirely different, both as regards isomer shift and quadrupole splitting. It is therefore easy to discern the appearance of one oxidation state in the

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