

## Lattice Vibrations in Vanadium

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### *Abstract*

The phonon dispersion curves, frequency spectrum and specific heat of vanadium have been calculated on the basis of the lattice dynamical model of Sharma and Joshi (1963). The frequency distribution has been derived according to Blackman's (1937, 1955) root-sampling technique by the numerical sampling of 192 000 frequencies corresponding to 64 000 points considered in the first Brillouin zone. This computed frequency distribution has then been used to calculate the lattice specific heat of vanadium. The resulting values of the specific heat have been compared with experimental measurements in terms of the Debye characteristic temperatures. The theoretical results for the phonon dispersion curves, frequency spectrum and specific heat are found to be in reasonable agreement with experimental data.

### **Introduction**

Although the dispersion curves of the transition elements niobium (Nakagawa and Woods 1963) and tantalum (Woods 1964) of Group Vb were determined nearly a decade ago by inelastic neutron spectrometry, it was only recently that the phonon dispersion relations for the remaining element of the group, namely vanadium, were measured by Colella and Batterman (1970) by means of the thermal diffuse scattering of X-rays. The phonon dispersion relations for vanadium could not be studied by the conventional neutron scattering techniques because of its almost totally incoherent scattering cross section. On the other hand, this unusual feature allowed a rather direct measurement of the phonon frequency spectrum by incoherent inelastic neutron spectrometry and, as such, the frequency spectrum of vanadium was extensively investigated by this technique (Brockhouse 1955; Carter *et al.* 1956; Stewart and Brockhouse 1958; Eisenhauer *et al.* 1958; Turberfield and Egelstaff 1962; Chernoplekov *et al.* 1963; Haas *et al.* 1963; Pelah *et al.* 1963; Zemlyanov *et al.* 1963; Gläser *et al.* 1965; Mozer *et al.* 1965; Roy *et al.* 1967; Page 1967). There were also theoretical attempts by Singh and Bowers (1959), Alers (1960), Sharan (1962), Hendricks *et al.* (1963) and Clark *et al.* (1964) to calculate the frequency spectrum of vanadium. All these previous studies reveal some interesting and puzzling features about the frequency distribution function of vanadium. Most of the theoretical and experimental investigations disagree as to the location and intensity of the peaks in the frequency spectrum. Although several of the experimental spectra are qualitatively similar they differ in many details. In addition, some of the experimental results show a high-energy tail which is difficult to explain theoretically.

The theory of lattice vibrations in crystals (Born and Huang 1956) has progressed a long way since the early work of Born and von Kármán (1912) but the interatomic forces are so intricate that it is difficult to solve lattice dynamical problems in an

exact way and it is usually convenient to resort to approximate models (see e.g. Joshi and Rajagopal 1968). Sharma and Joshi (1963) have proposed a semi-phenomenological model for the lattice dynamics of cubic metals by considering a central interaction between the nearest and next-nearest ions and an electron-ion interaction arising from the compressibility of the electron gas. The volume-dependent force due to the compressibility of the electron gas and its interaction with ions is computed by an average over the Wigner-Seitz sphere. This concept of averaging the volume-dependent electronic force over the Wigner-Seitz sphere was first used by Laval (1963). In fact, the basic proposals of the so-called Sharma-Joshi model were outlined earlier by Laval, although he made no attempt at their application. However, this model has furnished a plausible interpretation of the lattice dynamical behaviour of a number of cubic alkali metals (Gupta 1966*a*; Pal 1970, 1972), noble metals (Gupta 1966*b*, 1968; Gupta and Sharma 1967) and transition metals (Pal 1971; Pal and Gupta 1966*a*, 1966*b*). In fact, the Sharma-Joshi model has been found to be of quite general application and also of practical utility because of its simplicity and straightforward physical interpretation.

As the phonon dispersion relations in vanadium have not yet been studied on the basis of any of the existing central force-constant models (de Launay 1953; Bhatia 1955; Krebs 1965; Chéveau 1968), it was thought of interest to employ the simple model of Sharma and Joshi (1963) in the calculation of these dispersion curves. The fact that the various existing theoretical models fail to adequately account for the frequency distribution function of vanadium also indicated the need for further consideration of the lattice vibrational spectrum. The results of calculations of the phonon dispersion relations, the frequency distribution function and the specific heat of vanadium on the basis of the Sharma-Joshi model are presented below.

## Theory

The secular equation determining the angular frequencies  $\omega$  of the normal modes of vibration of a cubic metal can be written as (Sharma and Joshi 1963)

$$|D(\mathbf{q}) - m\omega^2 I| = 0, \quad (1)$$

where  $m$  is the mass of the atom and  $I$  is a  $3 \times 3$  unit matrix. The elements of the dynamical matrix  $D(\mathbf{q})$  for a body-centred cubic crystal are given by

$$D_{ii}(\mathbf{q}) = 8\alpha_1(1 - C_1 C_2 C_3) + 4\alpha_2 S_i^2 + 4q_i^2 a^3 K_e G^2(qr), \quad (2a)$$

$$D_{ij}(\mathbf{q}) = 8\alpha_1 S_i S_j C_k + 4q_i q_j a^3 K_e G^2(qr), \quad (2b)$$

where

$$S_i = \sin(q_i a), \quad C_i = \cos(q_i a), \quad G(x) = 3(\sin x - x \cos x)/x^3,$$

$2a$  is the lattice parameter of the cubic cell,  $r$  is the radius of the Wigner-Seitz sphere,  $q_i$  is the  $i$ th cartesian component of the phonon wave vector  $\mathbf{q}$ ,  $K_e$  is the bulk modulus of the electron gas, and  $\alpha_1$  and  $\alpha_2$  are the central force constants for the nearest and next-nearest neighbours. The parameters  $\alpha_1$ ,  $\alpha_2$  and  $K_e$  can be parameterized in terms of the three independent elastic constants of a cubic metal as

$$\alpha_1 = ac_{44}, \quad \alpha_2 = a(c_{11} - c_{12}), \quad K_e = c_{12} - c_{44}. \quad (3)$$

### Numerical Computations and Discussion

The force constants appearing in the secular equation have been estimated from the data for the room temperature elastic constants given by Alers (1960). The numerical values of these constants and the other parameters of vanadium used in the present calculations were:

Elastic constants ( $10^{11}$ dyn $\text{cm}^{-2}$ )			Lattice parameter $2a$	Density $\rho$
$c_{11}$	$c_{12}$	$c_{44}$	( $\text{\AA}$ )	( $\text{g cm}^{-3}$ )
22.795	11.870	4.255	3.028	6.022

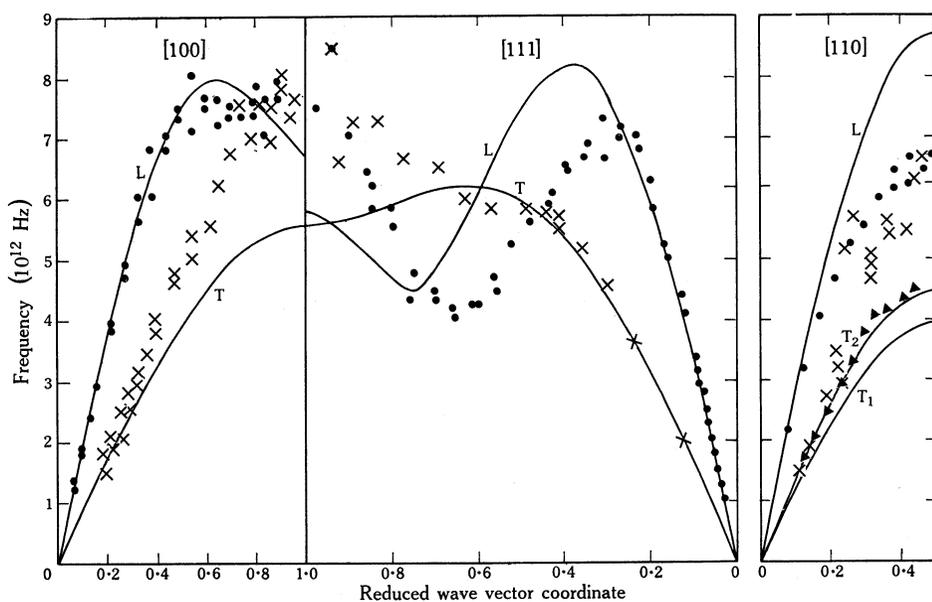
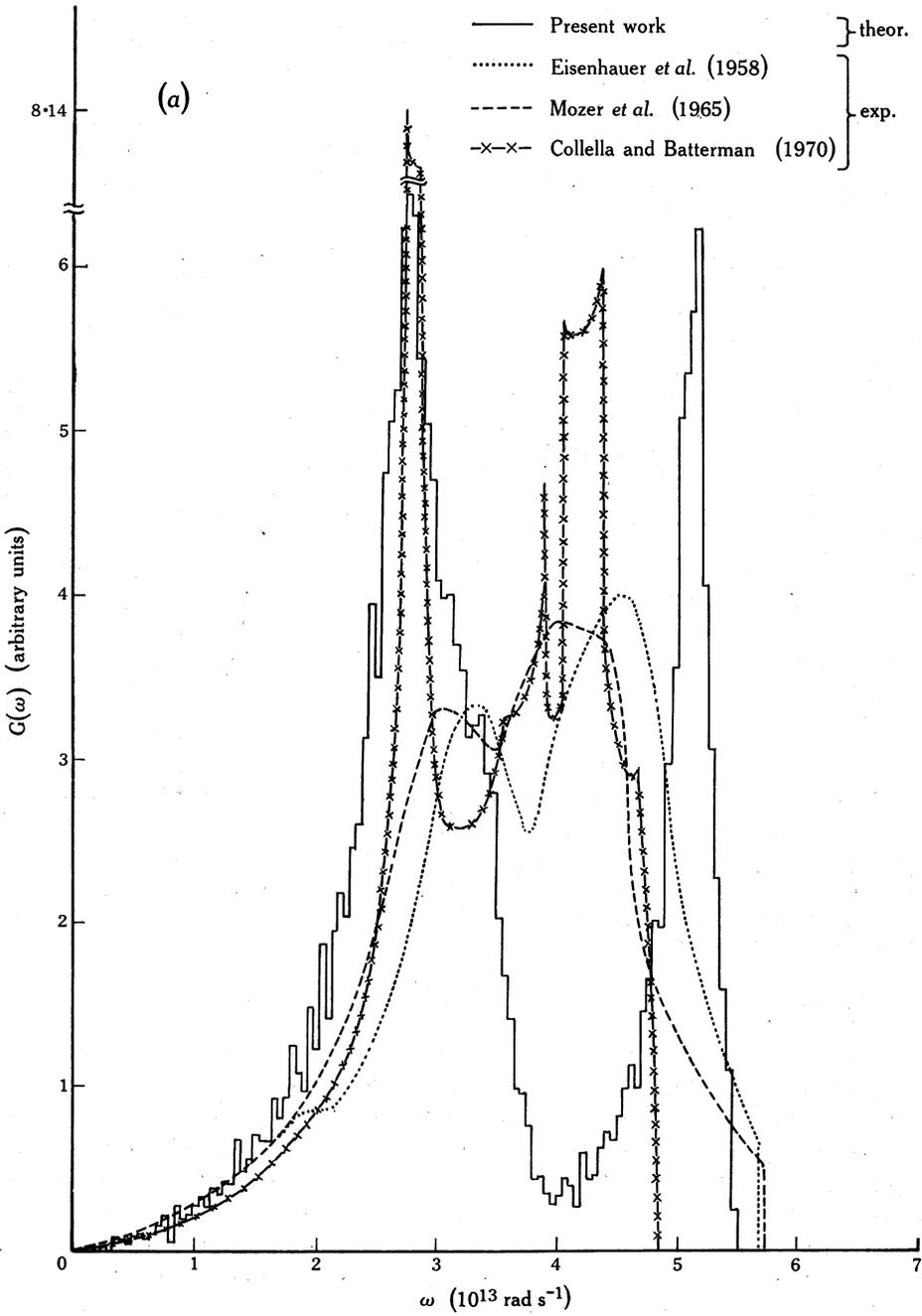


Fig. 1. Phonon dispersion relations for the longitudinal (L) and transverse (T) modes along the indicated three major symmetry directions in vanadium. The present theoretically calculated curves are compared with the experimental points obtained by Colella and Batterman (1970) from thermal diffuse scattering of X-rays.

#### Dispersion Curves

The theoretically calculated frequency versus wave vector dispersion relations along the major symmetry directions of vanadium together with the X-ray thermal diffuse scattering data of Colella and Batterman (1970) are plotted in Fig. 1. It can be seen that the theoretical curves are in poor agreement with the experimental data except for low values of the reduced wave vector, and the discrepancy between the results increases with increasing wave vector. The theoretical curves do not show any sign of the somewhat intriguing overlapping and crossing over of the experimental longitudinal and transverse modes along all the symmetry directions. Although the technique of thermal diffuse scattering of X-rays for the study of lattice vibrations is not as sophisticated and accurate as neutron spectrometry, the results of Colella and Batterman in the low frequency region seem to be quite reliable, since the thermal scattering is high here and the extra contributions are a small fraction of the total measured intensity. However, much reliance cannot be put on their measurements



Figs 2a and 2b. Comparison of theoretical and experimental results for the frequency spectrum of vanadium.

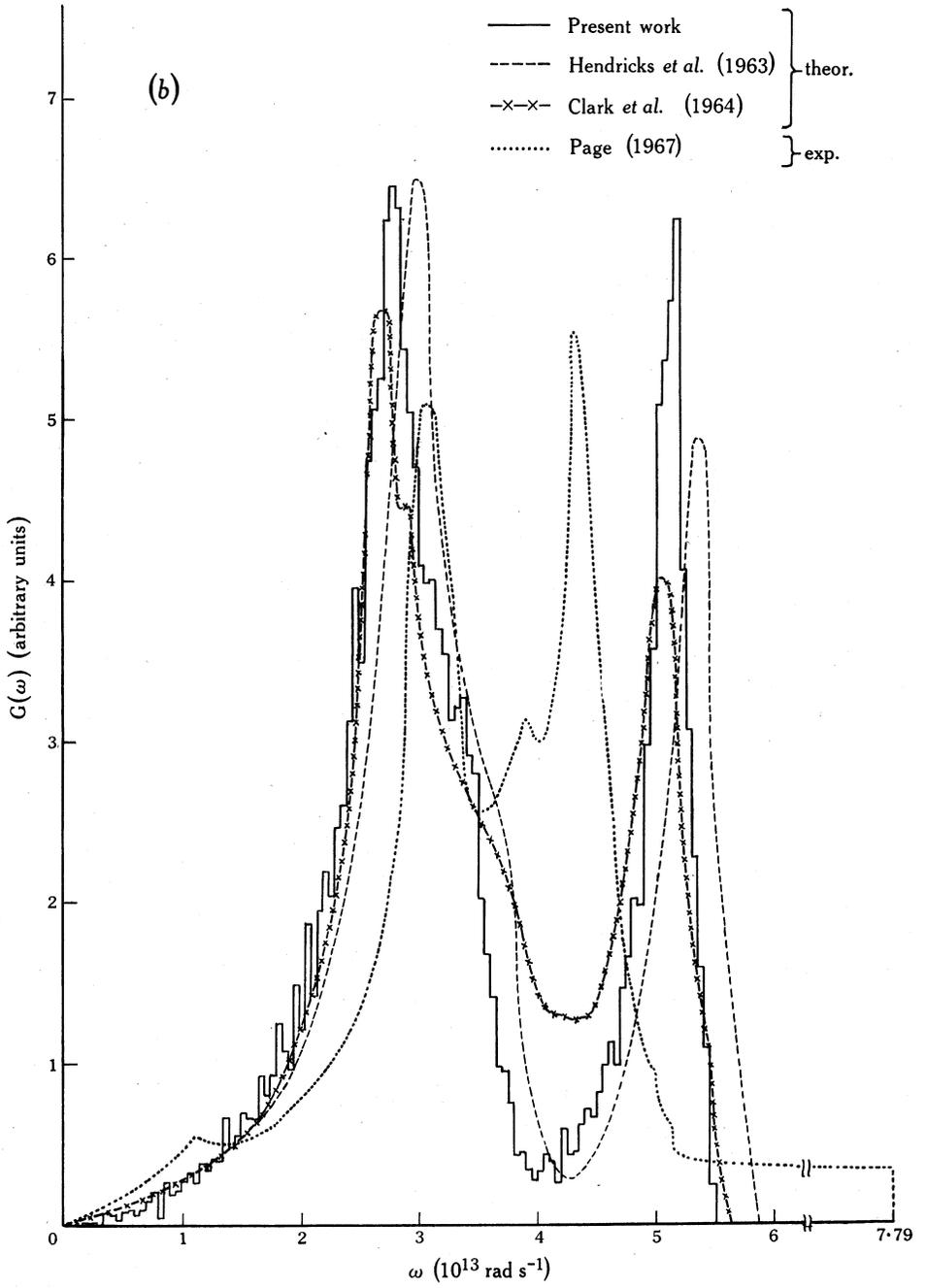


Fig. 2b

for large values of the wave vector. The fact that the calculated phonon dispersion curves for vanadium do not satisfy the symmetry requirements of a cubic lattice at certain points manifests the inherent drawback of the Sharma–Joshi model which results from the averaging of the electronic contribution over the Wigner–Seitz sphere.

### *Lattice Frequency Spectrum*

The frequency distribution has been computed by the numerical sampling of frequencies (Blackman 1937, 1955) over a discrete subdivision in the wave vector space. The reciprocal space was divided into miniature cells with axes one-fortieth of the length of the reciprocal lattice cell and the vibration frequencies were calculated from the roots of the secular determinant for 1661 wave vectors in the irreducible portion of the first Brillouin zone. Each point was weighted according to the number of points symmetrically equivalent to it; the importance of giving correct weights to points has been emphasized by Sayre and Beaver (1950) and Dayal and Sharan (1960). The total number of points in the whole zone was thus  $40^3 = 64\,000$ , and the total number of frequencies 192 000. In order to calculate the frequency distribution function  $G(\omega)$ , counts of the number of frequencies falling in intervals of  $0.05 \times 10^{13}$   $\text{rad s}^{-1}$  were used to construct a frequency histogram.

As noted in the Introduction, there have been many experimental investigations of the frequency distribution of vanadium by incoherent inelastic neutron spectroscopy. Recently Colella and Batterman (1970) have also measured the frequency spectrum by employing the technique of thermal diffuse scattering of X-rays. Of the several theoretical attempts to calculate the spectrum, Singh and Bowers (1959) used the hypothetical elastic constants deduced from low temperature specific heat data (these hypothetical constants deviate considerably from the experimentally measured values) and calculated the frequency distribution function on the basis of the noncentral three force-constants model. The calculation of Alers (1960) based on the central two force-constants model of Montroll and Peaslee (1944) does not agree with experiment and is open to the criticism that the model used represents an extreme over-simplification and only allows a description of the general features of the observed distribution. This same model was employed by Clark (1960), who arrived at a conclusion similar to Alers. Sharan (1962) computed the frequency spectrum on the basis of the lattice dynamical model of de Launay (1953) but he also failed to obtain satisfactory agreement with experiment. Further calculations were made by Hendricks *et al.* (1963), who employed a noncentral three force-constants model, and by Clark *et al.* (1964) from a noncentral four force-constants model.

An overall comparison of the various theoretical and experimental frequency spectra of vanadium as shown in Figs 2*a* and 2*b* reveals some interesting features. The theoretical curves differ from the experimental ones with regard to the location and intensity of the two peaks, the theoretical maxima being widely spread and sharp with less intensity at the higher frequency, while the experimental maxima tend to be flat and more intense at the higher frequency. The neutron scattering experiments of Turberfield and Egelstaff (1962) and Page (1967) also show that the spectrum has a tail at high frequencies (Fig. 2*b*), which is not expected theoretically. All the theoretical and experimental studies show a two-peak characteristic function, although the measurements of Page (1967) indicate an additional intermediate peak that is not discernible in any other experimental results. Page claims to have discovered this small

central peak because of much better resolution in his experimental technique. A further small low energy peak (at about  $\omega = 1.25 \times 10^{13} \text{ rad s}^{-1}$ ) has been observed experimentally by Pelah *et al.* (1963) and Page (1967). Peretti *et al.* (1962) put forward theoretical arguments for the possible existence of low energy peaks in the frequency spectrum associated with the Kohn effect.

It can be seen from Figs 2a and 2b that the present calculated frequency spectrum of vanadium does not show, as expected, any evidence of the high energy tail observed by Page (1967) and Turberfield and Egelstaff (1962), nor does it exhibit any sign of the small central peak found only by Page (1967). However, the calculation does agree closely with the theoretical result of Hendricks *et al.* (1963). The computed frequency histogram of vanadium corroborates the earlier finding by the author (Pal 1972) regarding the relative location and magnitude of the two peaks in the lattice vibrational spectra of monatomic cubic metals.

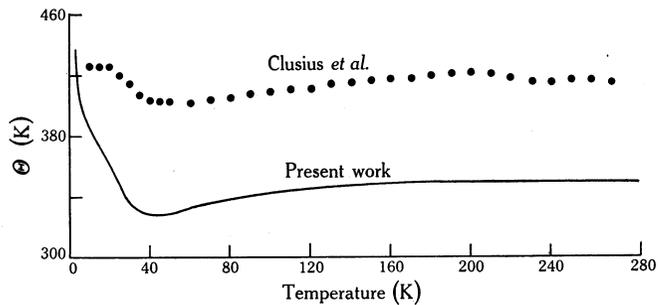


Fig. 3. Comparison of the present theoretical curve with the results derived from the experimental data of Clusius *et al.* (1960) for the variation of the Debye temperature  $\Theta$  with temperature.

### Lattice Specific Heat

The contribution of lattice vibrations to the thermodynamic properties depends solely upon the frequency distribution function  $G(\omega)$ , and having obtained this function one can easily calculate the lattice specific heat at constant volume  $C_v$  from the relation

$$C_v = k_B \int_0^{\omega_{\max}} \{x^2 e^x / (e^x - 1)^2\} G(\omega) d\omega,$$

where  $x = \hbar\omega/k_B T$  and the other symbols have the usual meaning. Using the derived frequency spectrum, the lattice specific heat per gram atom has been computed by the numerical integration of this expression. The values of the specific heats at different temperatures have been compared with the calorimetric data by computing the equivalent Debye characteristic temperatures  $\Theta$ , and the results are shown in Fig. 3. The experimental specific heat data for vanadium have been taken from the measurements of Clusius *et al.* (1960) and corrected for the electronic contribution, as indicated by those authors. It can be seen from the figure that, although the theoretical  $\Theta$  versus  $T$  curve qualitatively agrees with the experimental data, the computed  $\Theta$  values are uniformly lower than experiment throughout the temperature range studied.

## Conclusions

The discrepancies between the theoretical results and the experimental data can be ascribed to the approximate calculation of the electron–lattice interaction and to the assumption of the short-range nature of the interionic interactions. Analyses of the experimental phonon dispersion curves of the transition metals indicate that the interatomic forces in these metals are of a fairly long-range nature. It may be noted that the transition elements are characterized by incomplete d-shells (Mott 1962, 1964) which are expected to play a significant role in the lattice dynamics of these metals. The pronounced asphericity of the charge density and the finite overlap of 4s electrons would lead one to expect large changes for the transition metals. However, it emerges from the present study that although the simple model of Sharma and Joshi (1963), which considers central interaction between the nearest and next-nearest neighbours only, does not provide detailed agreement with experiment it nevertheless gives a general description of the lattice vibrations in vanadium.

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