

$$\begin{aligned}
 A_0(-\nu) &= A_0(\nu) \\
 r(K, t-s) &= \left\{ -\frac{K^2}{12\pi^2} \int 2(1-\cos\nu u) Y_0(\nu) \right. \\
 &\quad \left. [Y_0(\nu) + 2iA_0(\nu)] e^{i\nu(\tau-\sigma)} d\nu \right\} \\
 &\quad \times \exp \left[ \frac{iK^2}{2\pi} \int (1-\cos\nu u) (Y_0 + iA_0) d\nu \right] \quad (\text{B3})
 \end{aligned}$$

This will make a contribution to  $G_1(\tau-\sigma)$ . It is already in the form of a Fourier transform so for the contribution to  $G_1(\nu)$  we omit the integral on  $\nu$  and the factor  $e^{i\nu(\tau-\sigma)}$ . According to (29) we must next multiply  $r(K, t-s)$  by  $y(\omega_K, u) + ia(\omega_K, u)$  and integrate on  $u$ . This is best done by dividing the range of  $u$  from 0 to  $\infty$  and from  $-\infty$  to 0, and in the latter putting  $u \rightarrow -u$  so that all integrals are over positive  $u$  only.

The integral in the exponent is  $-K^2/2$  times

$$\begin{aligned}
 &-\frac{i}{\pi} \int (1-\cos\nu u) [Y_0(\nu) + iA_0(\nu)] d\nu \\
 &= +i[\mathbf{Y}_0(u) + \mathbf{Y}_0(-u)] + 2[\mathbf{A}_0(0) - \mathbf{A}_0(u)] \quad (\text{B4})
 \end{aligned}$$

[where  $\mathbf{Y}_0(t)$ ,  $\mathbf{A}_0(t)$  are the inverse transforms of  $Y_0(\nu)$ ,  $A_0(\nu)$ ]. Expression (46) is equal to  $D(u)$ , defined in (35c) for  $u > 0$ , and  $D(-u)$  for  $u < 0$ , since  $\mathbf{Y}_0(u) = 0$  for  $u < 0$ . Thus, this term in  $r(K, t-s)$  contributes a piece

$$\begin{aligned}
 &-\frac{K^2}{3\pi} Y_0(\nu) [Y_0(\nu) + 2iA_0(\nu)] \\
 &\quad \times \int_0^\infty (1-\cos\nu u) [y(\omega_K, u) + y(\omega_K, -u) \\
 &\quad + 2ia(\omega_K, u)] e^{-\frac{1}{2}K^2 D(u)} du. \quad (\text{B5})
 \end{aligned}$$

Adding the three other corresponding pieces from  $\exp\{i\mathbf{K} \cdot [\mathbf{X}'(t) - \mathbf{X}'(s)]\}$ , etc., multiplying by  $|C_{\mathbf{K}}|^2$ , and integrating over  $K$  [see Eq. (30)] gives the first term in (35). The second term is gotten in an analogous way from  $\Phi_0$ . We need to expand our expression for  $r(K, t-s)$  just to first order in  $K^2$ . The terms like  $e^{-\frac{1}{2}K^2 D(u)}$  are replaced by one. The resulting expression is an integral on  $u$ ,  $\int_0^\infty (1 - e^{i\nu u}) S_0(u) du$ , where

$$S_0(u) = \text{Im} C \left( e^{i\nu u} + \frac{2 \cos \nu u}{e^{\beta \omega} - 1} \right) = C \sin \omega u.$$

The integral on  $u$  gives  $C\nu^2/w(\nu^2 - w^2)$ , as in the last term of (34).

## Phonon Frequency Distribution in Vanadium at Several Temperatures

K. C. TURBERFIELD AND P. A. EGELSTAFF

*Atomic Energy Research Establishment, Harwell, England*

(Received December 4, 1961; revised manuscript received April 18, 1962)

The energy spectrum of a beam of 4 Å neutrons scattered by vanadium has been measured using a conventional time-of-flight technique. Analysis of the results using the methods described by Placzek and Van Hove has been carried out to determine the frequency distribution of phonons in vanadium. The sample was held at 206, 300, and 860°K, and the effect of temperature on the phonon spectrum was observed.

The lower part of this spectrum is not "Debye" in form, but the departures from this simple shape become less at increasing temperatures. The upper peak in the phonon spectrum previously observed is relatively insensitive to temperature. A high-energy tail to the observed neutron spectrum is discussed; it is probable that this indicates a tail to the phonon distribution, which previous measurements at room temperature had failed to reveal.

### 1. INTRODUCTION

SINCE Born and von Kármán<sup>1</sup> published their theory of vibrations in crystal lattices, considerable attention has been devoted to the calculation of the distribution of frequencies and the variation of specific heat with temperature. Blackman<sup>2</sup> has given a review of the techniques of calculation, the results of the calculations, and their comparison with measured specific heat curves. Recently, frequency distributions have been

studied by neutron scattering techniques which allow much more detailed information to be obtained than with the older methods. Scattering data obtained using vanadium can be interpreted without difficulty, as the scattering is almost entirely incoherent. This material has been the subject of experiments by Stewart and Brockhouse<sup>3</sup> and by Eisenhauer *et al.*<sup>4</sup> Unfortunately (as discussed below), these experiments lack the pre-

<sup>1</sup> M. Born and T. von Kármán, *Physik Z.* **13**, 297 (1912).

<sup>2</sup> M. Blackman, *Handbuch der Physik* (Springer-Verlag, Berlin, 1955), Vol. 711, p. 325.

<sup>3</sup> A. T. Stewart and B. N. Brockhouse, *Revs. Modern Phys.* **30**, 250 (1958).

<sup>4</sup> C. M. Eisenhauer, M. I. Pelah, D. J. Hughes, and H. Palevsky, *Phys. Rev.* **109**, 1046 (1958).

cision necessary to give much more than a qualitative comparison with theory. It is the purpose of this paper to describe a more detailed series of experiments on vanadium in which substantial improvements were made and in addition the important feature of temperature dependence was examined.

Van Hove<sup>5</sup> has discussed the mechanism through which discontinuities in the slope of the frequency distribution arise. He has shown that these correspond with the existence of maximum, minimum, and saddle points in the dispersion relationship between frequency and wave number of the thermal waves of a lattice. A change in the slope of the dispersion relationship at these points may produce large changes in the value of the frequency distribution. This effect has been considered by Squires<sup>6</sup> in the case of aluminum and by Hardy and Karo<sup>7</sup> in the case of sodium chloride. These authors show by numerical examples how the position, shape, and size of the peaks in the frequency distribution depend sensitively upon the crystal model employed, and that in practice, the frequency distribution is at least as important as the dispersion law in testing crystal models.

The important regions of the frequency distribution correspond to the maximum frequencies of the transverse or longitudinal branches of the dispersion law. The maximum frequency for transverse vibrations has generally been found to occur near the center of the range for longitudinal vibrations. Since the latter contribution will vary approximately as  $\nu^2$  in this range, the data will be presented as the ratio  $\rho(\nu)/\nu^2$ , thus making the longitudinal component nearly constant and making the peak in the transverse component easily visible. It is unfortunate that both the earlier experiments on vanadium involved large corrections in this sensitive region. It will be explained in Sec. 3 how in the present experiment these corrections have been greatly reduced.

In addition to this defect, the earlier experiments also involved large corrections at the highest frequencies (i.e., the limiting frequencies for longitudinal vibrations), and, accordingly, care was taken in this experiment to obtain improved data in the high-frequency range. These data have shown up a possible high-frequency tail to the distribution which is not easily explicable on present theories.

## 2. THEORY

Placzek and Van Hove<sup>8</sup> have discussed a practical method of measuring the frequency distribution using the technique of (incoherent) scattering of cold neutrons. The intensity of neutrons scattered through a given angle

<sup>5</sup> L. Van Hove, Phys. Rev. **89**, 1189 (1953).

<sup>6</sup> G. L. Squires (private communication).

<sup>7</sup> J. R. Hardy and A. M. Karo, Phil. Mag. **5**, 859 (1960); A. M. Karo, J. Chem. Phys. **31**, 1489 (1959); J. R. Hardy, Phil. Mag. **4**, 1278 (1959).

<sup>8</sup> G. Placzek and L. Van Hove, Phys. Rev. **93**, 1207 (1954).

is measured as a function of the energy transfer, and after allowing for certain corrections, the intensity of scattered neutrons is proportional to the number of phonons, and the energy transferred is proportional to their frequency. Vanadium is the ideal material to use in this experiment, since its scattering is 99% incoherent. The formula of Placzek and Van Hove includes one-phonon effects only, but it can easily be extended to include multi-phonon effects (see, for example, Squires<sup>9</sup>).

If the frequency distribution is assumed to be the same for waves of any polarization, the cross section including multi-phonon terms reads:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial \beta} = \frac{\sigma}{4\pi} \frac{k}{k_0} e^{-\beta/2} e^{-\alpha\lambda} \left[ \delta(\beta) + \alpha I_1(\beta) + \frac{\alpha^2 I_2(\beta)}{2!} \dots \right]. \quad (1)$$

$k_0$  and  $k$  are the wave numbers of the incident and scattered neutrons, respectively.  $\alpha = \hbar^2 Q^2 / 2Mk_B T$ , where  $Q = \mathbf{k}_0 - \mathbf{k}$ .  $\beta$  is the energy transferred, in units of  $k_B T$ .  $\alpha\lambda$  is the Debye-Waller factor.

$$I_1(\beta) = \rho(\beta) / 2\beta \sinh(\beta/2);$$

$$I_n(\beta) = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} I_1(x_1) I_1(x_2) \dots I_2(x_n) \times \delta(\beta - x_1 - x_2 \dots x_n) dx_1 dx_2 \dots dx_n. \quad (2)$$

$\rho(\beta)$  is the required one-photon spectrum and can be obtained from the inelastic scattered neutron spectra when the multi-phonon contributions are subtracted.

In calculating the multi-phonon processes, the average over-all propagation directions is usually taken before the integrals  $I_2, I_3, \dots$  of Eq. (1) are evaluated. More strictly this order should be reversed, the one-phonon spectrum being split into longitudinal and transverse components in the ratio of one to two. The two-phonon contributions calculated in this way are given by the formula

$$I_2 = \int_{l=0}^{l=1} \left\{ \int_{-\infty}^{+\infty} [l^2 I_L(x) + (1-l^2) I_T(x)] \times [l^2 I_L(\beta-x) + (1-l^2) I_T(\beta-x)] dx \right\} dl,$$

where the suffixes  $L$  and  $T$  identify the longitudinal and transverse components. Examples of  $I_2$  obtained by subdivisions of simple functions are given in Fig. 1. It can be seen that the reversal of the order of direction averaging and integration can result in an enhancement of the two-phonon contribution at certain energies, but can also reduce it at others, and has little effect on the general level. Therefore, although Eq. (2) is not strictly accurate it appears to be reliable for the calculation of the multi-phonon corrections to the experimental data.

<sup>9</sup> G. L. Squires, Proc. Roy. Soc. (London) **A212**, 192 (1952).

3. EXPERIMENTAL DETAILS

The experimental arrangement is shown in Fig. 2. A neutron beam is taken from the DIDO reactor and filtered through a block of beryllium metal held at a temperature of 90°K. After filtering, the beam consists mainly of neutrons with wavelengths  $>3.95 \text{ \AA}$ . A rotating chopper of the type described by Egelstaff *et al.*<sup>10</sup> is placed in the filtered beam and has the effect of pulsing the beam and of allowing only those neutrons, whose velocities lie within a narrow band, to remain in the beam. This chopper is made of magnesium/cadmium alloy and has three narrow curved slots cut across a diameter. It is rotated at a speed of 37 500 rpm, and at this speed the optimum transmission occurs for a neutron wavelength of 4  $\text{ \AA}$  and the full width at half-height of the wavelength spectrum passed by the chopper is  $\sim 20\%$ . However, the Be filter removes the upper half of this spectrum to reduce this width to  $\sim 10\%$ . Because of the narrow bandpass of the chopper, any of the shorter wavelength neutrons which are not removed by the filter will be absorbed in the chopper, so that the beam of neutrons falling upon the sample will be very clearly defined in wavelength.

The sample of vanadium is placed in the beam at a

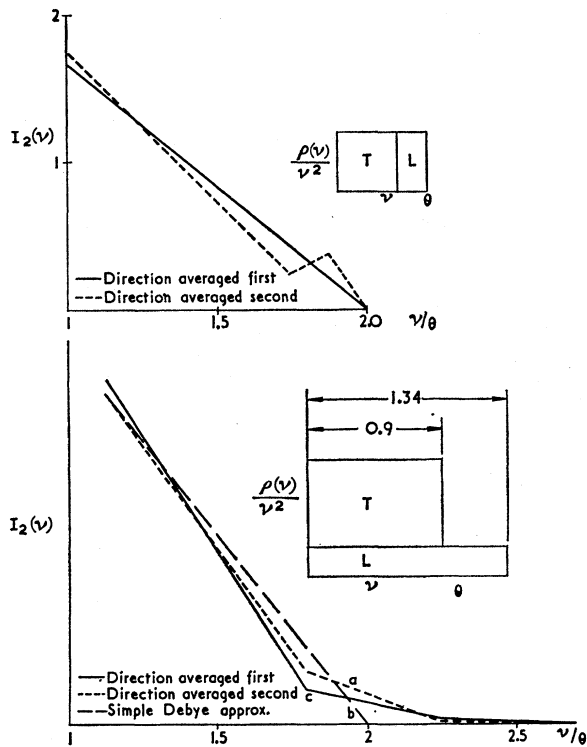


FIG. 1. Illustration of the changes in the two-phonon cross sections produced by inverting the order of the direction averaging and convolution integrals.

<sup>10</sup> P. A. Egelstaff, S. J. Cocking, and T. K. Alexander, *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1961).

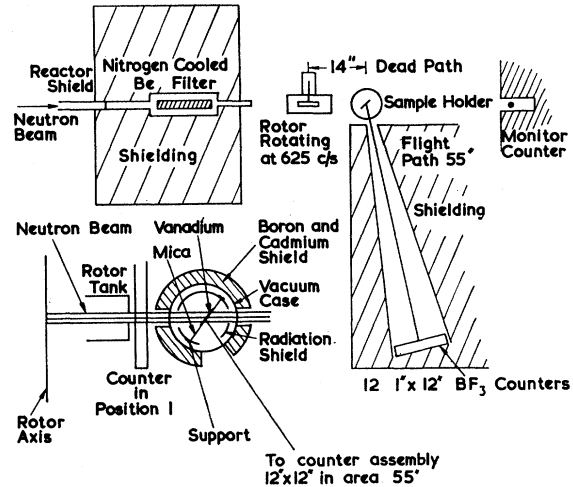


FIG. 2. Layout of the experimental apparatus. The left-hand bottom inset shows the detail of the sample assembly.

point 14 in.<sup>11</sup> from the center of the chopper. It was 3/16 in. thick  $\times 2\frac{1}{2} \times 1\frac{1}{2}$  in., and was clamped across the beam, its ends being attached to a mica support by vanadium clamps. These ends were wound with nichrome wire insulated with mica for the hot measurements. (This arrangement was used also for the room-temperature measurements). A 4½-in.-diam cylinder of 5/1000-in. steel foil acted as a radiation shield round the sample. Windows were cut in this to avoid scattering the incident and outgoing neutrons. Copper bars sheathed in cadmium were used as sample supports for the cold measurements, and these bars terminated in a reservoir of ethyl alcohol and dry ice. In all measurements the sample was contained in an evacuated cylindrical stainless steel vessel of 6-in. diam with 15/1000-in.-thick walls. A shielding "muff" of borated resin clad in cadmium surrounded the vacuum vessel closely, holes being cut into it to give access for the straight-through neutron beam and for the scattered beam in the direction of the counters. These holes ensured the final collimation so that the beam fell upon the specimen only and not its supporting clamps or heaters, and also that scatter from the entrance and exit windows of the vacuum vessel could not reach the counters.

Twelve 1-in. diam, 12 in. long, enriched BF<sub>3</sub> counters placed side by side formed a 12-in.-sq. detector which was held to face the scattered beam at 55 in. from the

<sup>11</sup> This unfortunately allows the neutron pulse length to be considerably broadened out due to the long flight time of these very slow neutrons over this distance. At the center of the chopper, the pulse is about 10  $\mu\text{sec}$  wide at half-height, whereas at the sample it is about 25  $\mu\text{sec}$  at half-height. The advantage of placing the chopper before the sample lies first in the high purity of the resulting neutron beam and, secondly, for this experiment, in the fact that the scattered neutrons can pass without attenuation to the counter. The latter point is important for the purposes in mind, since if the chopper were placed in the scattered beam it would modify the shape of the neutron energy spectrum, necessitating further corrections.

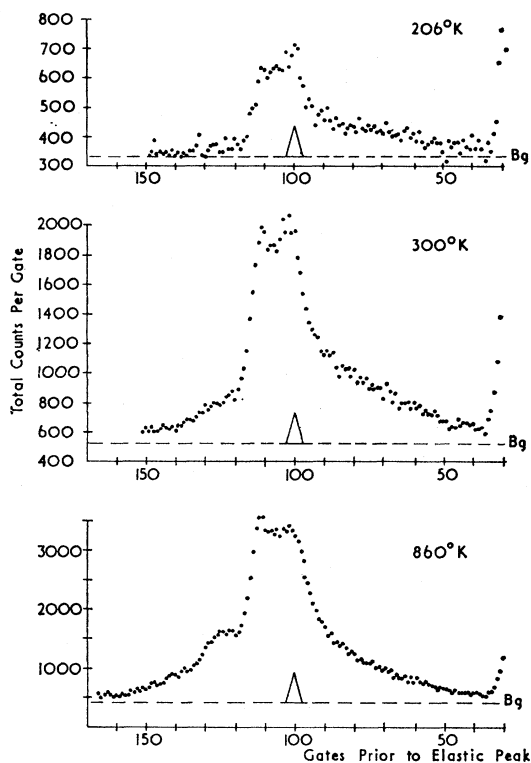


FIG. 3. The observed counts vs time-of-flight channel number for the scattering of 4 Å neutrons by vanadium at 206, 300, and 860°K.

sample center. The mean angle of scatter was  $75^\circ$ , and the sample was held in the transmission position bisecting the supplement of the angle of scatter. The counters were mounted in a cadmium-lined tunnel which tapered towards the sample and so again prevented any but direct sample scattering from reaching the counter. The tunnel ended within 1 in. of the vacuum vessel, and was closed with a 10/1000-in. aluminum foil; the air thus trapped in the long flight path was dried with silica gel. The flight path was further surrounded by 3 ft of polythene granules mixed with  $B_2O_3$  powder.

The time-of-flight spectra were measured by a 200-channel tape recorder and analyzer, 8- $\mu$ sec gates being used.<sup>12</sup> Also an A.E.R.E. hundred-channel analyzer (type 1524) was used for some measurements to provide a check on the tape analyzer. The incident neutron beam velocity distribution was measured by recording the time-of-flight spectrum of the incident neutron beam at a counter placed between the rotor and the sample container (at 5.5 in. from the sample center) and also by recording the spectrum of elastically scattered neutrons at the main counter assembly. Both measurements used a pulse derived from the rotor drive shaft as the time origin.

<sup>12</sup> F. H. Wells, *Nuclear Instr.* **2**, 165 (1958).

A cadmium sheet was placed between the rotor and sample for 5 min in every 15 min by means of an automatic movement, and the time-of-flight spectra for each condition recorded on separate channels of the tape recorder, it being well suited for this type of use. In this way the background counts could be integrated over the length of the measurements. To insure that no time-dependent scattering came from the sample surroundings, a count for two days was made with no sample. The spectra observed with the cadmium shutter in and out of the beam were time independent and equal in count rate over the range of time-of-flight of interest.

A chart recorder was used to record the count rate of a monitor counter placed in the beam trap of the apparatus (see Fig. 2). Also recorded were the outputs of two Chromel-Alumel thermocouples clamped to the sample. If the temperature of the sample had drifted by more than the allowed limits which are given below, it was simple (by counting up the 15-min periods of the spectrum measurements during which this had occurred) to reject the relevant measurements during the subsequent analysis of the "exposed" recording tape.

For the cold measurements the allowed temperature drift of the sample was within the limits 203 to 213°K. At 860°K the maximum temperature differential across the sample was 15°K.

#### 4. ANALYSIS OF DATA

The observed time-of-flight spectra are given at Fig. 3(a) to (c). It will be seen that their interesting features are the temperature dependence of the peaks and the high-energy region.

In calculating the true time-of-flight spectrum from these results, certain corrections must be applied to them. The sample scattered 15% of the incident beam and absorbed a further 38%. Multiple scattering occurs in the sample and can be shown to contribute about 1 to 2% of the single inelastic scattering count rate at the "cutoff" of the inelastic spectrum at room tempera-

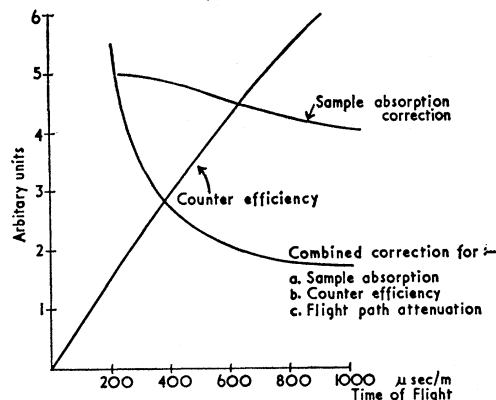


FIG. 4. Relative values of correction factors for miscellaneous effects.

ture. This correction is less than that made by Stewart and Brockhouse<sup>3</sup> and by Eisenhauer *et al.*<sup>4</sup> in similar experiments, as they used thicker samples, of 3/8 in. and 1/2 in., respectively, as compared with our 3/16 in. Our correction was calculated assuming isotropic scattering and should be accurate to ~20%. To check this result the correction for Stewart and Brockhouse's condition was recalculated and compared with their quoted correction. Reasonable agreement was obtained.

Because the absorption cross section varies significantly across the inelastic spectrum energy range, a correction must be applied for the attenuation occurring to the scattered neutrons in the sample. The absorption cross section of the sample was checked by a "pile oscillator" measurement, giving  $4.9 \pm 0.4$  b for neutrons of 2200 m/sec in agreement with the value of 4.98 b quoted in BNL-325.<sup>13</sup> Air scattering in the flight path also necessitates a small correction. Counter efficiency was calculated from the stated pressure, enrichment and sizes of the counter and the boron content checked at 0.025 eV and 0.067 eV by a neutron transmission measurement. These corrections are shown in Fig. 4.

The background counts were calculated from the integrated measurements as described. As the sample is placed after the rotor, no chopper function correction is needed. Also, because the chopper and filter combine to produce a narrow "line" spectrum for the incident neutrons, the corrections for incident energy spread are negligible. The experimental arrangement was chosen so that there was a negligible chance of neutrons which had lost energy to the sample being recorded at the same time as those neutrons which had gained energy. For example, neutrons suffering an energy loss equivalent to 0.07 of the Debye temperature have the same apparent time-of-flight as those suffering an energy gain of twice the Debye temperature. However, the intensity of the slower neutrons would be less than 2% of the background (Fig. 3).

In order to determine whether the purity of the sample affected the results, certain tests were carried out on the actual samples used after the neutron experiments had been completed. A spectroscopic and chemical analysis gave the results in Table I. These figures show that iron and oxygen are the only significant

TABLE I. Analysis of vanadium sample (accuracy  $\pm 10\%$ ).

Fe	Al	Si	Mn	Mg	Cu	
0.2	0.06	0.04	0.005	Trace	Trace	wt%
C	N	H				
740	370	15	ppm by wt			
O						
0.24 wt % (sample with the surface removed)						
0.28 wt % (sample including the surface)						

<sup>13</sup> D. J. Hughes and R. B. Schwartz, *Neutron Cross Sections*, Brookhaven National Laboratory Report BNL-325 (Superintendent of Documents, U. S. Government Printing Office, Washington, D. C., 1957).

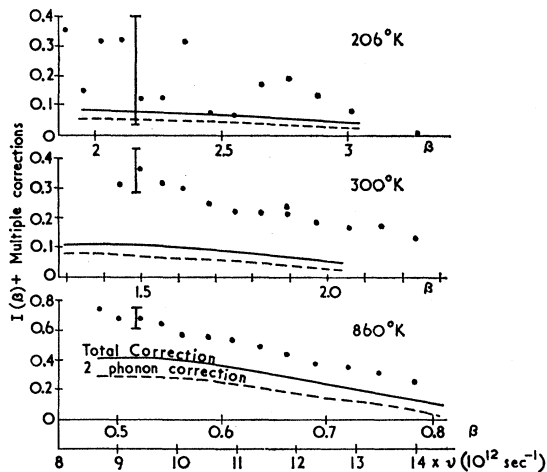


Fig. 5. Comparison of theoretical calculations and experimental data in the region where the two-phonon term is important (the error bars include statistical and systematic errors).

impurities and that some oxygen occurs in the surface film. An x-ray analysis showed this film to be predominantly VO.

The effect of oxygen in the vanadium lattice is to increase the lattice parameter and make the specimen harder. An x-ray determination of the lattice parameter was made for the sample used and for an unused piece obtained from the original sample. This showed that the lattice parameter had increased from 3.0275 to  $3.0325 \pm 0.001$  Å during the experiment. The results of Seybolt and Samsion<sup>14</sup> show that this increase indicates a 0.5 at. % oxygen increase which is in agreement with the chemical analysis figure of 0.24 wt %. Also the Brinell hardness was found to be ~210 which further indicates that the amount of dissolved oxygen is ~0.2 to 0.3 wt %. In addition, a metallographical examination showed the presence of ~1 at % of grains in a second phase. It is thought that these are vanadium carbide and are too big to strain the parent lattice.

No correction has been attempted for the oxygen or carbon contamination, but it is expected to have a small effect on the phonon distribution.

Finally, corrections are necessary for the multi-phonon terms in Eq. (1). However, first an absolute scale for the data is found by the normalization of the frequency distribution, i.e.,  $\int \rho(\beta) d\beta = 1$ . This normalization implies that the multi-phonon corrections have been made so that in practice a reiterative procedure is adopted.

As a first step a two-phonon function was calculated using the Debye model assuming a "Debye temperature" of 340°K as indicated by other measurements.<sup>15</sup> This function was then compared with the high-energy tail shown in the data in Fig. 5. It was found that the

<sup>14</sup> A. U. Seybolt and H. T. Samsion, *J. Metals* **5**, 292 (1953).

<sup>15</sup> W. S. Corak, B. B. Goodman, C. B. Satterthwaite, and B. Wexler, *Phys. Rev.* **102**, 656 (1956).

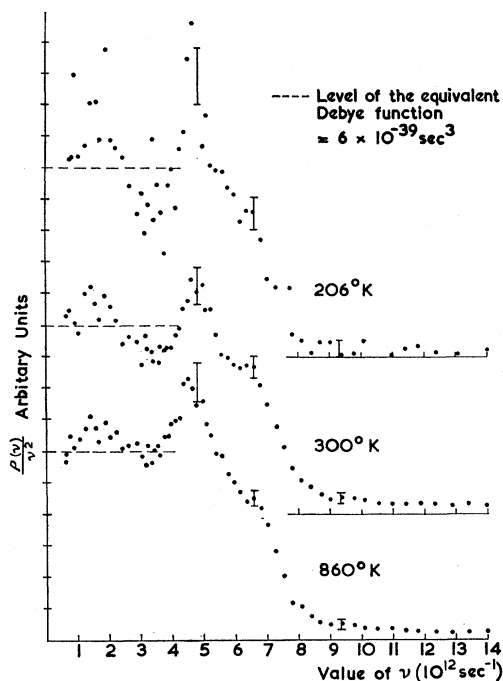


FIG. 6. Deduced values of the frequency distribution of vanadium at three temperatures (the error bars include systematic and statistical errors).

two-phonon correction was roughly only  $\frac{1}{3}$  of this high-energy region for the 206 and 300°K cases and about  $\frac{1}{2}$  of it in the 860°K case. The three-phonon and subsequent terms are much less than the two-phonon term due to the small value of the momentum transfer parameter. The combined statistical uncertainty and other errors of measurement (as shown in the figures) are too small to account for this except possibly in the 206°K case.

The size of the two-phonon term depends upon the shape of the one-phonon term. Thus, the possibility was considered that discontinuities in the true one-phonon spectrum (as predicted by Van Hove<sup>5</sup>) may give rise to sharp peaks. The finite resolution of these measurements (as well as those of previous workers) could round off such peaks in the one-phonon region and also more readily round off the resulting peaks in the two-phonon region, where resolution effects are greater. The two peaks observed in the one-phonon spectrum may be higher and narrower in proportion, with a similar result in the two-phonon term. However, it can easily be shown that the total two-phonon function  $\int I_2(\beta) d\beta$  is independent of the shape of the one-phonon term  $I_1(\beta)$  provided  $\int I_1(\beta) d\beta$  is constant [this condition is equivalent to keeping the Debye temperature approximately constant and less than the sample temperature while varying the shape of  $\rho(\beta)$ ]. The net result which can be produced by this effect is to alter the general amplitude of the two-phonon term by 10 to 20%; this is insufficient to account for the above discrepancy.

The magnitude of the high-energy tails in Fig. 3 could be accounted for by assuming a lower Debye temperature of 280°K resulting in an increased two-phonon correction. However, this would be inconsistent with other data<sup>16</sup> and also with an effective Debye temperature (equivalent to  $\langle 1/\beta^2 \rangle$ ) calculated from the observed frequency distribution. Thus, the observed high-energy tail cannot be attributed to multiple processes, and at least part of it probably corresponds to a real tail on the frequency distribution.

Renormalization including this contribution from the high-energy region leads to a "Debye temperature" of 380°K, and the final two-phonon contribution is calculated to about 5% accuracy from the assumed one-phonon spectra, while the higher phonon terms are calculated using a simple Debye model with this Debye temperature.

The observations are well accounted for using this assumption, up to an energy transfer of twice the Debye temperature, and beyond this point the experimental results are no longer significant as statistical accuracy is low and systematic errors and resolution width become increasingly important.

The corrected one-phonon functions  $\rho(\nu)/\nu^2$  are given in Fig. 6 including a contribution from the high-energy tail. The peak occurring at the higher energy in the one-phonon time-of-flight spectrum occurs as a shoulder on this function.

No correction is made for the finite resolution width of the apparatus.

## 5. DISCUSSION

A comparison of the reduced data obtained at the different temperatures is given in Fig. 6 and shows that the general shape of the frequency distribution of

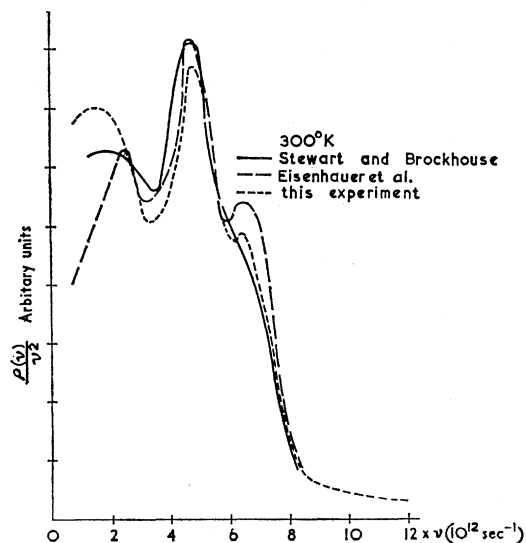


FIG. 7. Comparison of three measurements of the frequency distribution of vanadium at room temperature.

vanadium is independent of temperature, thus confirming the assumption normally employed in solid-state theory. However, there do appear to be changes occurring which are on the limit of detection in the present experiment. The variations which were apparent in the time-of-flight data of Fig. 2 have largely disappeared in the corrected data of Fig. 6. This is due to the behavior of the correction factors and indicates that a high accuracy in both the experimental measurements and the corrections will be necessary before the exact variation of frequency distribution with temperature is established.

On the other hand, a detailed comparison of the parts of Fig. 6 indicates that the three peaks in the frequency distribution broaden as the temperature is increased. This is in accordance with expectations. The resolution width of the equipment is such as to prevent corrections being made without knowing the shape of these peaks. However, numerical comparisons can be made on the basis that the shape of the peak is essentially independent of temperature. In this case the trough at  $\nu \approx 3.5 \times 10^{12}$ /sec decreases in magnitude (expressed as the differences between the minimum amplitude and the maximum on either side) by a factor of about  $2\frac{1}{2}$  between 200 and 800°K.

In Fig. 7 we give a comparison of the room temperature data uncorrected for resolution reported here with that reported earlier.<sup>3,4</sup> This shows that the general features observed in the various experiments are in agreement. However, in our work the corrections were smaller (e.g., thinner samples, smaller angle of scatter, no rotor-function correction, better defined incident energy spectrum, etc.), and the time-of-flight resolution was better than in the case of Stewart and Brockhouse.<sup>3</sup>

Discrepancies between the measurements at the low-energy peak may be largely due to resolution broadening and poor statistical accuracy. Relatively good agreement occurs over the central region containing the other two peaks of the frequency distribution. However the high-energy tail shown in our results was not reported by either Stewart and Brockhouse,<sup>3</sup> or Eisenhauer *et al.*<sup>4</sup> The latter measurement did reveal a similar effect but the presence of a thermal contamination in the incident beam prevented further discussion. The data of Stewart and Brockhouse<sup>3</sup> suffered from "frame overlap" which made the true background level vary rapidly in this high-energy region. They used a different technique to

find the true level, and these factors might account for this discrepancy. On the other hand, it is possible but unlikely that this tail arises from the small oxygen content of our sample. The earlier workers did not report analytical details about their samples, so that comparison is difficult for this reason too.

Lattice imperfections, or distortions, or the presence of impurities, could introduce a number of high-frequency modes into the spectrum, and if this were so, the magnitude of the tail would vary from sample to sample of metal. Alternatively, the tail may represent a true lattice effect possibly due to the conduction electrons. A repetition of the experiments with different sample purities would be worthwhile to confirm the existence of the high-energy region of the phonon spectrum and to investigate its properties.

The conclusions of these measurements are that there is evidence for a high-energy tail to the one-phonon spectrum which has not been observed in the previous observations at room temperature. The lower region of the one-phonon spectrum is not "Debye" in form and also shows some temperature dependence.

It should now be profitable to compare predictions based on models of the vanadium lattice with our observations although further improvements in experimental precision are probably still necessary for a detailed comparison. Such calculations have been attempted by Singh and Bowers,<sup>16</sup> but unfortunately the elastic constants they used have been shown to be incorrect by the more recent work of Alers.<sup>17</sup> A new calculation also covering temperature dependence is clearly worthwhile.

#### ACKNOWLEDGMENTS

It is a pleasure to acknowledge the help of L. V. Lewis, B. Booty, V. Rainey, A. Wraight, and G. Peckham in the construction of the apparatus and the recording of data and to acknowledge the cooperation of the DIDO Reactor Operations Staff.

We are indebted to C. E. Austing and F. T. Birks for arranging the chemical and spectroscopic analysis, to P. J. Oram for the pile oscillator measurements, to P. Madsen for the metallographic analysis, and to W. Baker for the x-ray investigations. D. Harris measured the transmission of the counters.

<sup>16</sup> D. N. Singh and W. A. Bowers, *Phys. Rev.* **116**, 279 (1959).

<sup>17</sup> G. A. Alers, *Phys. Rev.* **119**, 1532 (1960).